# RADIOLYTIC OXIDATION OF PROPANE

BY

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DEDICATED TO
MY PARENTS

Our experiments are not carried out to decide whether we are right, but to gain new knowledge. It is for knowledge's sake that we plow and sow.

R. Willstatter

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Abstract of Dissertation Presented to the Graduate Council of the University of Florida in partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

The Radiolytic Oxidation of Propane

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The Co-60 gamma radiolysis of gaseous propane was studied at 100 torr pressure and 25 °C, both pure and with 10% added oxygen. In the unscavenged system the major products and their G-values were hydrogen, 4.99; methane, 1.30; ethane, 1.95; iso-butane, 0.61; n-butane, 0.25; i-pentane, 0.42; n-pentane, 0.14; and hexanes, 0.89. Minor products were heptanes, 0.082; octanes, 0.067; nonanes, 0.088, and decanes, 0.033. Small yields of ethylene and propylene were also observed. Yields in the presence of 10% added oxygen were hydrogen, 1.87; methane, 0.83; and ethane, 1.22. Higher saturated hydrocarbons were eliminated.

In the presence of 10% oxygen, the major oxygen containing products and their G-values were acetone, 0.98; iso-propyl alcohol, 0.86; propionaldehyde, 0.43; n-propyl

alcohol, 0.11; acraldehyde, 0.14; and allyl alcohol, 0.038. Minor products were iso-butyl alcohol, 0.0085; n-butyl alcohol, 0.0029; tert-amyl alcohol, 0.0074; iso-amyl alcohol, 0.0013; and n-amyl alcohol, 0.0016. When the oxygen concentration was decreased below 5%, it was found that the yields of acetone, iso-propyl alcohol and n-propyl alcohol increased, propionaldehyde yield decreased and yields of other products remained constant.

The reaction scheme for formation of major products was examined using computer modeling based on 24 reactions in the unscavenged system and 28 reactions in the propane-oxygen system. Yields could be brought into agreement with the data within experimental error in nearly all cases, but in the pure propane system it was necessary to assume that the molecular hydrogen yield was accompanied by the deposition of polymer on the vessel wall.

# I. INTRODUCTION

Production of useful compounds by the chemical reactions taking place under the action of radiation is one of the important branches of atomic energy application. The radiation chemistry of propane is of special importance because it is the lowest normal alkane which provides both primary and secondary carbon atom sites. There have been a number of research papers published concerning the radiolysis of gaseous propane both with and without scavengers (1-23).

In 1926, Lind and Bardwell (1) reported the formation of product as heavy as pentane during the bombardment of propane gas with 6-Mev alpha particles from radon gas.

In 1952, Gevantman and Williams (2) made a study of the free radicals and their relative production in the radiolysis of propane with x-rays and electrons, but they did not report a complete product distribution. According to them in the radiolysis of propane, there was a distinct effect of the propane pressure. With increasing pressure the relative yield of the methyl decreased and the yield of methylene increased in such a fashion that the sum of the yields of methyl and methylene was approximately constant, and the yields of other radicals remained approximately

constant. To explain these two proposals were put forward:

1) Reaction of thermal methyl radicals with propane might produce methylene radicals.

$$CH_3^{\bullet} + C_3H_8 \longrightarrow CH_2 + H_2 + C_3H_7^{\bullet}$$

Since such reactions must be highly endothermic, this was not a satisfactory proposal.

2) Methyl and methylene radicals are both primary products of excited propane

$$C_3H_8^{*} \longrightarrow CH_3^{\bullet} + C_2H_4 + H^{\bullet}$$
$$\longrightarrow CH_2 + C_2H_6$$

A pressure effect on the relative efficiencies of these two processes was assumed.

In 1959, Yang and Manno (4) carried out the radiolysis of propane using gamma radiation and reported the identification of ten different compounds ranging from hydrogen to pentanes. After irradiation, the products were analyzed by gas chromatography. They also studied the effect of NO as a scavenger on the yields of various products. Assuming the $G(H_2)$ in propane to be 5.9, the product distribution relative to hydrogen yield was reported.

In 1960, Birdwell and Crawford (5) determined the primary products and their relative distribution in the gamma radiolysis of propane gas at low irradiation doses.

They identified compounds including hydrogen, hexanes, ethane, methane, iso-butane, isopentane, n-butane, and n-pentane; alkenes, such as propylene, ethylene etc. were indicated in the mass spectra of the irradiated propane samples, but their yields were too small for identification by gas chromatograph. These experiments were carried out at a pressure of 75 psi (388 cm) at a temperature of approximately 25 $^{o}$C using a Co-60 gamma source.

Birdwell and Crawford (5) were the first to identify hexanes in the gamma radiolysis of propane. They reported the product distribution relative to the hydrogen yield. No experiments were done by them using a scavenger. No mechanism was given by Birdwell and Crawford or by any other previously mentioned authors for the formation of the various products in the radiolysis of gaseous propane.

In 1960, Back (6) carried out the gamma radiolysis of hydrocarbon gases at very low conversions and used ethylene/propylene as scavengers for hydrogen atoms and concluded that two-thirds of the hydrogen produced in the gamma radiolysis of ethane, propane, n-butane and n-pentane in the gas phase came from hydrogen atoms.

Among the most recent publications, the papers of Fujisaki et al. (22) and Gawlowski et al. (23) deal with special topics of primary processes of the hydrogen yield and impurity effects, respectively.

Many other previous workers on the propane system had provided information on specific aspects of the chemistry involved, including ionic fragmentation of propane (24-28); ion-molecule reaction chemistry (29-33); and decomposition of excited propane, studied by VUV photochemistry (14,34). Numerous ionic processes occur along with the radical/excited molecular reactions which contribute substantially to certain product yields. A sequence of elementary reactions was observed which lead to $C_3H_8^+$ and $C_3H_7^+$ as stable ions (33). In the mass spectrum of propane three ions constitute over 60% of the total ionization (18) $C_2H_5^+$ (30.5%), $C_2H_4^+$ (13.1%) and $C_2H_3^+$ (12.3%). The proposed route is

$$\begin{aligned} C_3H_8^+ &\longrightarrow C_2H_5^+ + CH_3\cdot \\ &\longrightarrow C_2H_4^+ + CH_4 \\ &\longrightarrow C_2H_3^+ + H_2 + CH_3\cdot \end{aligned}$$

The work of Bone, Sieck, and Futrell (20) gives a broad overview of propane radiolysis with emphasis on ionic processes and noble gas sensitization.

In the analysis of oxygenated products it is necessary to find out what products are formed in the pure propane system and how the yields of these products are affected when a scavenger such as oxygen is added. It would be useful to report our data and compare it to previous work and carry out a computer analysis of the proposed reaction

scheme, which may be of interest in relation both to the earlier work and to our subsequent investigation of the oxygen scavenged system (35).

Oxygen has frequently been used as a free radical scavenger in the gamma radiolysis of both liquid and gas phase hydrocarbon systems (36). Most workers have recorded only the effect of oxygen in decreasing the yields of various hydrocarbon products formed in the unscavenged system. It is generally assumed that the portion of each product yield eliminated in this way is due to free radical reactions. In most instances, no attempt was made to characterize and measure the oxygen-containing products which are formed in the presence of oxygen. Molecular oxygen is an efficient acceptor for most organic radicals. A study of radiation chemical processes in organic systems in the presence of molecular oxygen allows one to ascertain the role of primary radicals in the basic mechanism of these processes, and at the same time opens new ways of producing oxidation products of practical interest (37). Some work has been published on the radiolytic oxidation of liquid hydrocarbons (38-51) as well as on gases (51-60), especially methane.

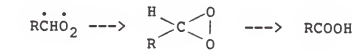
In 1926, Lind and Bardwell (1) irradiated mixtures of methane and oxygen with radon alpha rays. The end products of the reaction were reported to be carbon dioxide and

water. No attempt was made to identify any intermediate products, nor to establish a reaction mechanism.

In 1958, Mikhailov, Kyimora and Bogdonov (38) studied the irradiation of methane-oxygen mixtures with a beam of electrons produced at 112 kV. The oxygenated products identified were carbon monoxide, carbon dioxide, and water. The presence of peroxide, aldehydes, acids, and alcohols was shown by group reaction but these products were not characterized.

In 1959 Liebenthal, Albright, and Sesonske (43) irradiated mixtures of propane and oxygen in the temperature range of 350 $^{o}$C to 395 $^{o}$C at atmospheric pressure. The propane-to-oxygen mole ratios were 3:1, 5:1, and 10:1. The yields of formaldehyde, acetaldehyde and methanol increased significantly under gamma irradiation, sometimes as much as 100% - 200%.

In 1959 Bakh and T'ung T'ien-chen (52) investigated the formation of liquid products in the oxidation of n-heptane and n-nonane using x-rays over a temperature range of -80$^{o}$C to +130$^{o}$C. The acids formed were estimated by titration with sodium methylates in a nonaqueous medium. The scheme for the production of acid was as follows:



In 1961, Johnson and Salmon (39) reported the formation of methyl hydroperoxide in the radiolysis of methane in the presence of oxygen.

In 1962, Slavinskaya, Zhitneva, Kamenstskaya, and Pshezhetskii (46) described the kinetics of the chain oxidation of butane with oxygen under the action of fast electrons, and the characteristic features of the reaction mechanism, particularly the effect of the radiation on the branching of the reaction chain. The peroxides and aldehydes were determined polarographically. The scheme is based on processes which are most probable in thermal oxidation.

$$RH \longrightarrow R^{\bullet} + H^{\bullet}$$

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}$$

$$RO_2^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}$$

$$RO_2^{\bullet} \longrightarrow R_1HO + R_2O^{\bullet}$$

In 1965, Knox (47) proposed a mechanism for the low temperature oxidation of alkanes at 300 to 400 $^{o}$C where $HO_2^{\bullet}$ is converted to OH. radicals. This conversion involves a co-oxidation of the olefin AB, which is the primary oxidation product of most alkanes. The key to the conversion mechanism is the sequence shown:

$$AB \xrightarrow{HO_2} ABOOH \xrightarrow{O_2} OOABOOH \xrightarrow{HO_2} HOOABOOH \longrightarrow 2OH + AO + BO$$

In 1966, Hummel and Hearne (40) studied the radiolytic oxidation of methane. They reported the initial G-values of thirteen oxygenated and four hydrocarbon products for a mixture of 10% $O_2$ in methane over a range of pressures (1 to 76 cm Hg) and at two dose rates.

In 1968, Sochet, Sawerysyn, and Lucquin (48) studied the reaction of propane and oxygen at various pressures, temperatures, and concentrations. The analysis of some reaction products indicates an increase in the amounts of methane, ethane, acetaldehyde, ethyl alcohol, propyl alcohol, and especially iso-propyl alcohol and a decrease in the formation of hydrogen peroxide and olefin. All these results can be explained by radical reactions such as

$$R^{\bullet} + RO_2^{\bullet} \text{ (or } RO_2^{\bullet}) \text{ ---> ROOR ---> } 2RO^{\bullet}$$

$$\text{---> oxygenated products and } R^{\bullet} + R^{\bullet} \text{ ---> RR}$$

In 1978, Kunjappu and Rao (60) studied the radiation induced oxidation of n-heptane at 30 $^{o}$C using a Co-60 gamma source. They measured the yields of heptanols and heptanones; no acids were observed. Since 4-, 3-, and 2-heptanones are the only carbonyl compounds produced during the oxidation of n-heptane, this result suggests that added oxygen interferes with reaction pathways which lead to C-C bond rupture in an unscavenged system. Carbonyl and alcoholic products are formed by the decomposition of peroxy radicals through a disproportionation reaction between

them. Iodine and triphenyl methane (TRITAN) were used as scavengers. The scavenging reactions were represented as follows:

$$C_7H_{16} \longrightarrow C_7H_{15}^{\bullet} + H^{\bullet}$$

$$C_7H_{15}^{\bullet} + O_2 \longrightarrow C_7H_{15}O_2^{\bullet}$$

$$C_7H_{15}O_2^{\bullet} + C_7H_{15}O_2^{\bullet} \longrightarrow C_7H_{15}OH + C_7H_{14}O + O_2$$

$$C_7H_{15}^{\bullet} + \text{Scavenger} \longrightarrow \text{products}$$

According to Kunjappu and Rao, a fraction of the heptanones is formed by the direct interaction of the excited state with molecular oxygen.

$$C_7H_{16}^{*} \xrightarrow{O_2} C_7H_{14}O + H_2O$$

Below is a brief outline of the modern concept of the mechanism of hydrocarbon oxidation in the gas phase (36,61); the reaction pre-supposes the presence of alkyl radicals which are usually formed via thermal decomposition of an initiator. Oxygen readily adds to free radicals and if present will almost invariably play a part in radiation induced reactions. The combination of oxygen with radicals is easily understood if molecular oxygen is written as a diradical $^{\bullet}O\text{-}O^{\bullet}$ in recognition of its triplet-ground state (36). The product is a relatively stable peroxy radical.

$$R^{\bullet} + O_2 \longrightarrow R\text{-}O\text{-}O^{\bullet} \qquad (a)$$

A peroxy radical may abstract hydrogen from the substrate

$$RO_2^{\bullet} + RH \longrightarrow RO_2H + R^{\bullet} \qquad (b)$$

Reactions a and b together constitute a chain reaction of the type responsible for the autoxidation of a variety of organic compounds. Autoxidation is the slow oxidation of an organic compound by oxygen.

Combination of two peroxy radicals may give an organic peroxide

$$2RO_2^{\bullet} \longrightarrow R\text{-}O\text{-}O\text{-}R + O_2$$

but the products more often are two alkoxy radicals.

$$2RO_2^{\bullet} \longrightarrow 2RO^{\bullet} + O_2$$

At higher temperatures

$$RO_2^{\bullet} + RH \longrightarrow ROOH \longrightarrow RO^{\bullet} + OH^{\bullet}$$

Alkoxy radicals are more reactive than peroxy radicals and can abstract hydrogen from most organic compounds

$$RO + RH \longrightarrow ROH + R^{\bullet}$$

The combination of two alkoxy radicals to give a peroxide appears improbable relative to disproportionation to give an alcohol and carbonyl compound

$$2RCH_2O^{\bullet} \longrightarrow RCH_2OH + RCHO$$

Similarly, reactions between alkoxy radicals and an alkyl radical are less likely to give an ether ($RCH_2OR$) than a carbonyl compound and a hydrocarbon.

$$RCH_2O^{\bullet} + R^{\bullet} \longrightarrow RCHO + RH$$

According to Benson (62), olefins turn out to be more easily oxidized than alkanes. Allylic H atom abstraction leads to

$$CH_3CH{=}CH_2 + RO^{\bullet} \longrightarrow ROH + CH_2{=}CHCH_2$$
$$CH_2{=}CHCH_2 + O_2 \longrightarrow CH_2{=}CHCH_2OO^{\bullet}$$

We have selected propane as the most appropriate substrate for an investigation of radiolytic oxidation because it is the simplest species providing both primary and secondary carbon atom sites. Since no work was done previously to identify the products in propane-oxygen system, we thought it would be useful to identify the gamma ray oxidation products of gaseous propane and carry out a computer analysis of the proposed reaction scheme.

## II. EXPERIMENTAL METHODS AND EQUIPMENT

### A. Reagents and Their Purifications

Propane: Research grade (99.99%) propane obtained from Matheson Company was used. It was degassed by several freeze-pump-thaw cycles and stored in a vessel attached to the vacuum line. This material showed no observable impurities by flame ionization gas-chromatography.

Ethylene: Matheson Company C.P. grade (99.5%) ethylene was passed through a BaO drying tube into a storage vessel on the vacuum line. Possible air contamination was then removed by several freeze-pump-thaw cycles. Ethylene showed no observable impurities by flame ionization gas-chromatography.

Oxygen: Matheson Company Extra Dry (99.6%) oxygen was used as received from the manufacturer.

Other Reagents: Chemicals used for chromatographic calibration standards were used as received.

## B. Sample Preparation

Vacuum System: All samples for radiolysis were prepared on a vacuum line. The vacuum system used is shown in Figures 1 and 2. The pumping system was a Welch Duo-Seal pump connected through a liquid nitrogen trap to a two stage mercury diffusion pump. These pumps were connected to the main manifold through a second liquid nitrogen trap (X) and a stopcock ($V_1$). Attached to the main manifold were the following: a mercury manometer (M), a vacuum thermocouple gauge ($G_1$), inlets for propane and oxygen ($I_1$ and $I_2$), two storage bulbs ($B_1$ and $B_2$) and a Toepler pump-McLeod gauge apparatus Fig. 2. Teflon stopcocks (T) were used in the submanifold. Two stopcocks isolated the Toepler pump from the main manifold. A submanifold was provided to attach the radiolysis vessel (R) and sample loop ($S_1$) to the input of the combined Toepler pump-McLeod gauge system, via a liquid nitrogen U-trap packed with glass helices; this enabled the transfer of the radiolysis products to the sample loop ($S_1$) for analysis following irradiation. A special three-way stopcock allowed the Toepler pump to transfer non-condensible radiolysis products either into a series of calibrated volume (thus acting as a McLeod gauge) or into a sample loop ($S_2$) for analysis by gas-chromatography; an additional, custom tabulation on the base of the vacuum stopcock allowed

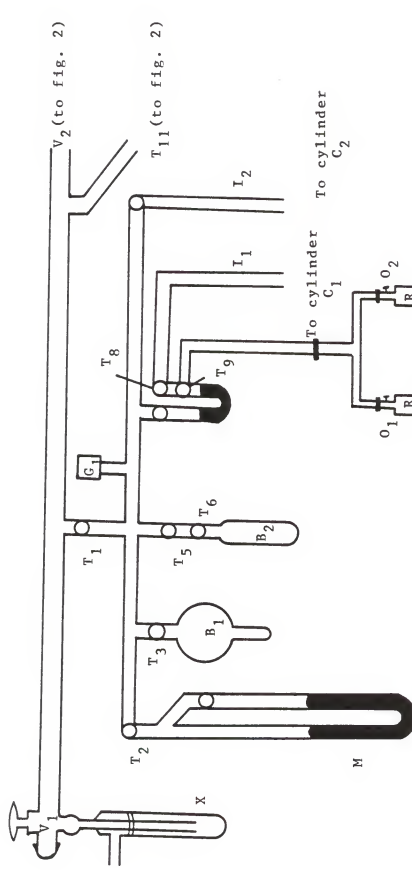



Fig. 1 Vacuum system

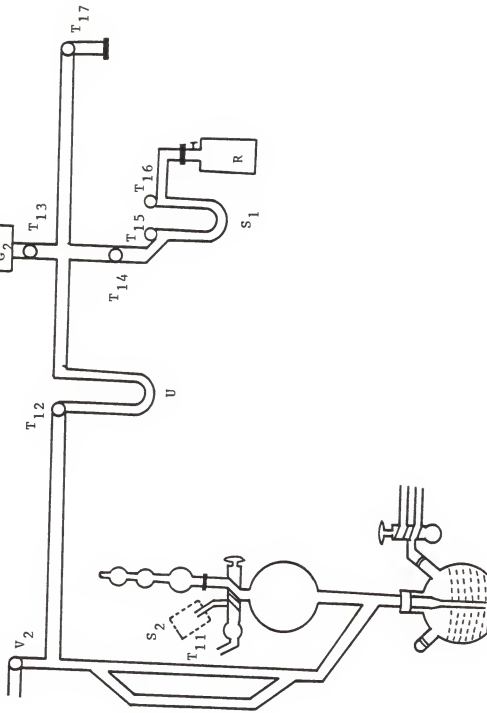



Fig. 2 Toepler Pump-Mcleod Gauge combination.

evacuation of the sample loop ($S_2$). This system was also equipped exclusively with Teflon stopcocks (T) and had a separate thermocouple vacuum gauge ($G_2$) for monitoring sample transfer operations.

Propane: Before each sample preparation, propane was transferred from cylinder ($C_1$) to the storage reservoir ($B_1$) and was de-aerated by repeated freeze-pump-thaw cycles until the thermocouple gauge indicated the absence of air. Valve $T_3$ was then closed and the condensed gas was brought to room temperature. Radiolysis vessels, having known volumes, were attached to $O_1$ and $O_2$. Valve $T_1$ was closed and valve $T_3$ was opened. The sample was allowed to expand into the radiolysis vessels (R). During the course of this operation, the pressure was monitored with a mercury manometer (M). At the desired pressure, valve ($T_3$) and the valves of the radiolysis vessels were closed and the excess material was condensed back into the storage vessel with liquid nitrogen by opening valve $T_3$. Knowing the temperature, pressure, and volume, the ideal gas law was used to calculate the amount of sample in the radiolysis vessels (R).

Propane with added Oxygen: Propane gas stored in the storage vessel ($B_1$) was de-aerated by repeated freeze-pump-thaw cycles and was brought to room temperature. A known amount of oxygen was taken in $B_2$ and then propane was added

to $B_2$, and the sample was allowed to mix. The desired amount of mixture was allowed to expand into the previously evacuated radiolysis vessels which were attached to $O_1$ and $O_2$. To ensure that the right amount of oxygen was taken, the reaction vessel was attached to the sample loop which was attached to the Toepler pump-McLeod gauge system as shown in Fig. 2. The cold trap and the sample loop were immersed in liquid nitrogen . Valve $T_{12}$ was closed and the valve of the reaction vessel was opened. Propane was allowed to condense in the sample loop and cold trap. The amount of oxygen was determined using the Toepler-McLeod apparatus. The amount of oxygen was also determined by gas chromatography after transferring the oxygen to the sample loop $S_2$.

## C. Sample Irradiation

Radiation Source and Vessel: Irradiations were carried out using a 300 curie Co-60 gamma ray source, which has been described previously (63). Figure 3 is a cross-sectional view of the irradiator. The decay scheme of Co-60 is shown in Fig. 4.

The helium arc welded nickel radiolysis vessel used is shown in Fig. 5. Two vessels were used, having volumes 108.5 cc. and 112.0 cc, respectively. The vessels were made of pure nickel having Hoke monel diaphragm valves

Legend: (A) counterweight; (B) upper support; (C) control rod handle; (D) extra top sheilding; (E) storage turret; (F) 300 curie Co-60; (G) shutter shown open; (H) rear wall; (I) door; (J) downward shielding; (K) door carriage (L) door crank; (M) door frame.

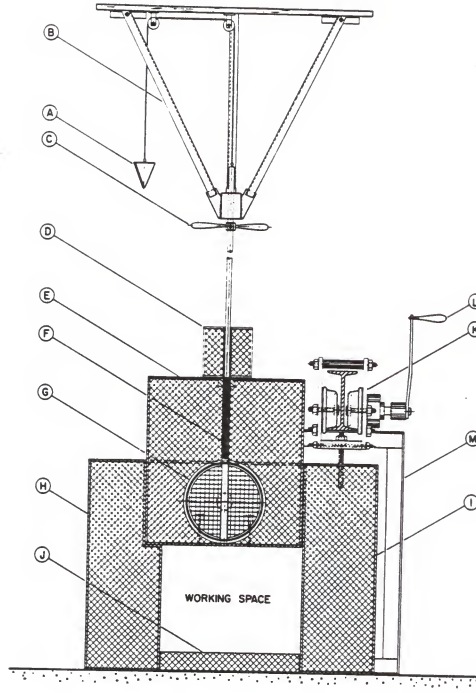



Fig. 3 Cross section of $^{60}Co$ gamma ray source

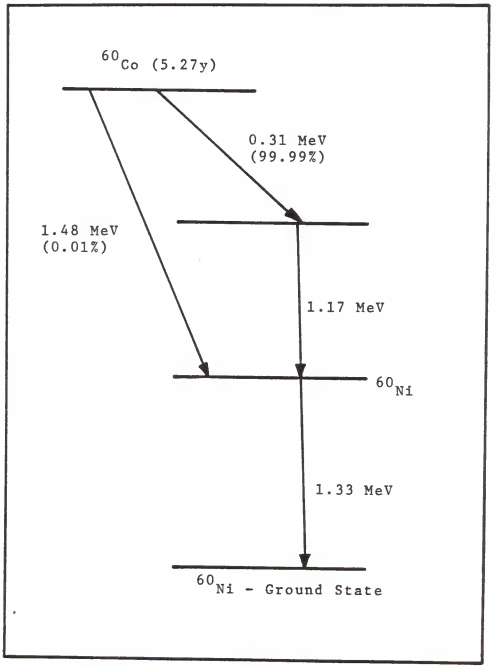



Fig. 4 Decay scheme for $^{60}$Co

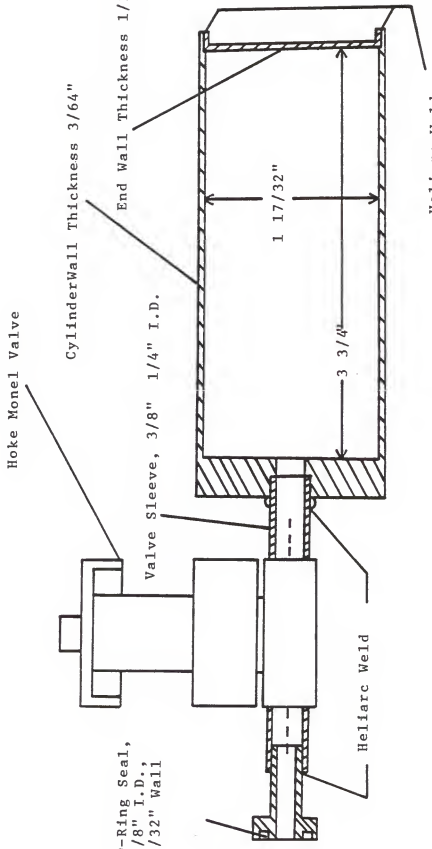



Fig. 5 Nickel vacuum tight radiolysis vessel.

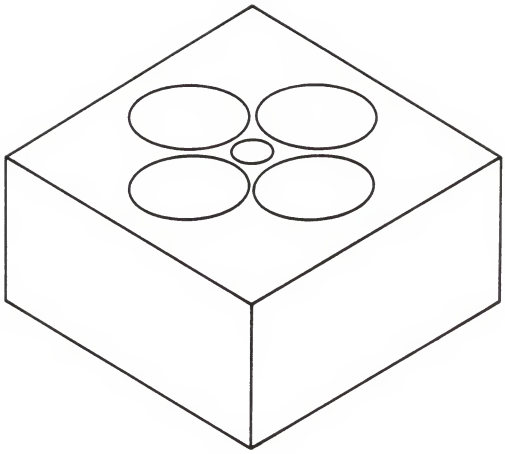


Fig. 6 Sample holder

(Hoke catalog No. 4611N4M). A rigid aluminum sample holder (Fig. 6) was used to assure reproducible positioning of radiolysis vessels.

## D. Dosimetry

Ethylene dosimetry was used to determine the absorbed dose rate of sample in the nickel vessel. It has been reported that the hydrogen yield in ethylene under gamma radiolysis in the pressure range of 150 to 1000 torr at room temperature is independent of the absorbed dose (64). The G value for hydrogen in ethelene dosimetry was taken as 1.2 (64,65). The absorbed dose rate in ethylene system was determined by measuring the hydrogen yield at room temperature, at irradiation times between 4 and 24 hours, and at a pressure of 300 torr. Following irradiation, the amount of hydrogen (along with small amounts of methane and ethylene) was determined using a Toepler-McLead apparatus. Knowing the total pressure, volume, temperature, and the quantities of methane and ethylene (determined by gas-chromatographic analysis), the hydrogen yield could be calculated. A plot of the hydrogen yield versus irradiation time gave a straight line as shown in Fig. 7. From the slope of the plot and the accepted G-value for hydrogen in ethylene (G = 1.2) the absorbed dose rate was determined. The absorbed dose rate for ethylene was 2.69 x

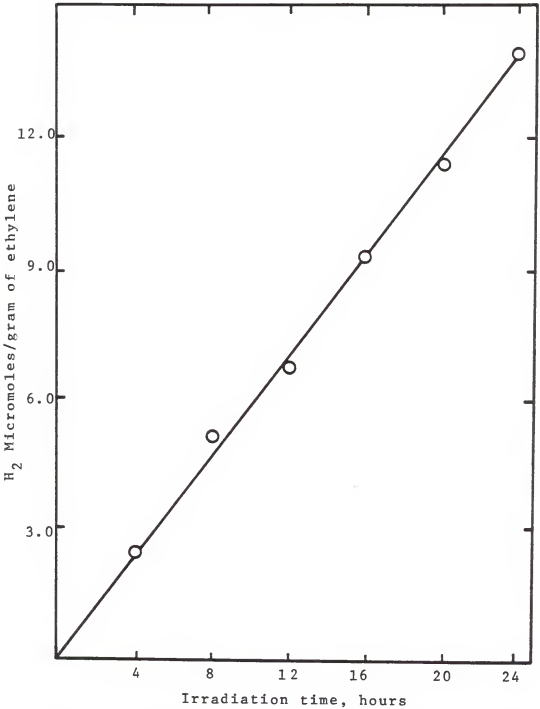



Fig. 7 Dosimetry: hydrogen yield from ethylene as a function of irradiation time.

$10^{19}$ eV/gh on December 18, 1979. This value was corrected for Co-60 decay during subsequent irradiations. Energy absorption in propane and propane-oxygen mixtures was calculated relative to the ethylene results. By application of the Bragg-Gray cavity principle (66), the ratio of the energy deposited per unit mass in the sample to that in the dosimeter can be determined by the ratio of these mass stopping powers (see appendix I). For mixtures of propane and oxygen it was assumed that each gas absorbed energy independently in proportion to the mass (more precisely the electron stopping power fraction) of that gas present. The dose rates obtained were $1.94 \times 10^{19}$ eV/gh for propane and $2.09 \times 10^{19}$ eV/gh for propane oxygen mixture.

## E. Analytical Equipment and Product Analysis

Gas Chromatograph Instrument: A Tracor model 1500 gas chromatograph equipped with a thermal conductivity detector and flame ionization detector connected in series was used for the qualitative and quantitative analysis of the organic products. A completely new injection box constructed in this laboratory using several commercial components was fitted onto the gas chromatograph. This is shown in Fig. 8. The input system included provision for the use of external sample loops, connected via a dual Swagelok fitting (obtained from Crawford Fitting Company,

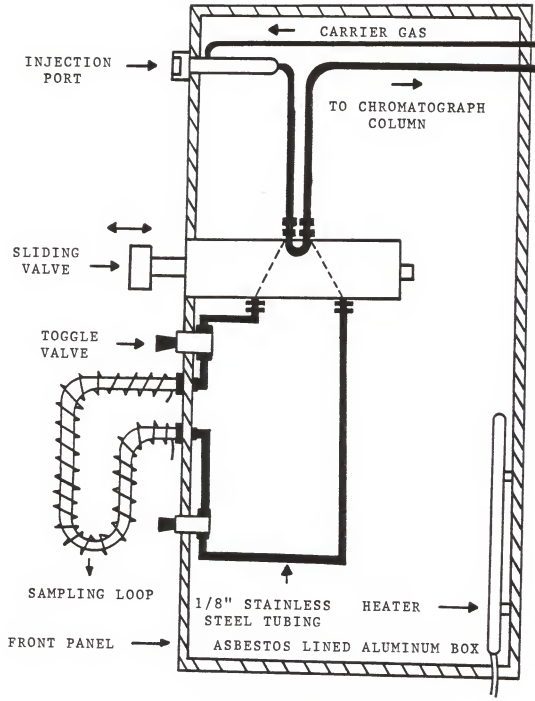



Fig. 8 Gas chromatograph sampling module.

Solon, Ohio). In this instrument, the gas chromatographic column is enclosed in an oven whose temperature was controlled by a multifunction programmer. The output of the gas-chromatographic detector was fed to a 1 mV potentiometric recorder. All the products were transferred on the vacuum line to the sample loops shown in Fig. 2 for injection into the gas chromatograph.

Analysis of Products Non-Condensible at -196 $^{o}$C:

After irradiation of the sample, the radiolysis vessel was attached to the sample loop ($S_1$) (Fig. 1Ø) which in turn was attached to a submanifold leading to the Toepler pump-Mcleod gauge apparatus. After a good vacuum had been reached, a zero pressure reading was taken with an Ealing Cathetometer. The system was isolated from the vacuum pumps and the valve of the nickel vessel was opened. The sample loop and the U-trap were immersed in liquid nitrogen. The non-condensible fraction was collected and transferred in twelve Toepler pump cycles to the McLeod gauge for measurement. The pressure reading was taken again. The gas was then transferred to the sample loop $S_2$ (Fig. 9) for flame ionization gas chromatographic analysis. This procedure allowed the determination of small quantities of $CH_4$ and $C_2H_4$ that contributed to the pressure measurement. Knowing the total pressure volume and temperature, the total moles of gas were calculated. Yields of $CH_4$

and $C_2H_4$ were determined by chromatographic analysis. From the total moles of gas and the moles of $CH_4$ and $C_2H_4$, the hydrogen yield was determined by difference.

Analysis of Condensible Organic Products: After the non-condensible gases were transferred to the sample loop $S_1$ (Fig.10), the liquid nitrogen Dewar was removed from the U-trap, and the gases were transferred to the sample loop $S_1$. The sample loop $S_1$ was then removed from the vacuum line and hooked to the gas chromatograph for analysis. In the analysis of hydrocarbons, all the products were separated on a 2.7m x 0.25 in O.D. stainless steel column packed with 60/200 mesh silica gel, with a nitrogen carrier gas whose flow rate was 40 ml/min. The oven compartment in which the column was situated was at room temperature 25 $^{o}$C. Programming was started 10 minutes after injection of the sample into the column. The oven compartment was programmed at a rate of 5 $^{o}$C/min up to a temperature of 200 $^{o}$C. At the end of each analysis, the column was conditioned at 200 $^{o}$C for several hours.

Prior to each analysis, the response of the flame ionization detector was determined using gaseous propane as standard. The flame ionization detector responses of the radiolysis products, relative to propane, are given in appendix III. Flame ionization detector is not sensitive to hydrogen. It was measured using a thermal conductivity detector.

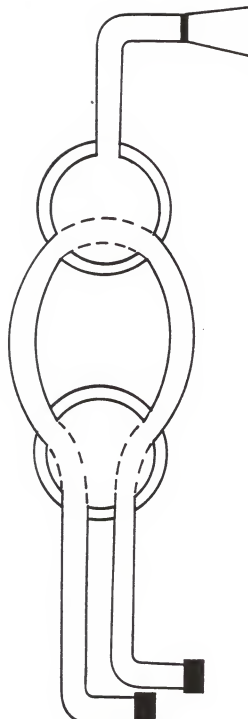


Fig. 9 Sample loop for non-condensible products.

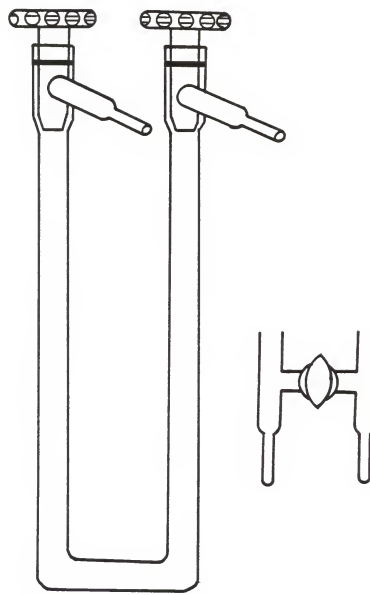


Fig.10 Sample loop for condensible products.

In the identification of the oxidation products of propane, a 6m long carbowax-20M (polyethylene glycol) column was used with a nitrogen carrier gas flow rate of 40 ml/min. The oven compartment in which the column is situated was heated to 60 $^{o}$C. Programming was started 20 minutes after injection of the sample into the column. The oven compartment was programmed at a rate of 4 $^{o}$C/min up to a temperature of 200 $^{o}$C. At the end of each analysis, the column was conditioned at 200 $^{o}$C for several hours.

Prior to each analysis, the response of the flame ionization detector was determined using acetone as standard. The flame ionization detector responses of the radiolysis products, relative to acetone, are given in appendix III.

In the oxidation of propane, a Porpak Q (a porous polymer composed of ethylvinylbenzene cross-linked with divinylbenzene to form a uniform structure of a distint pore size; type Q means non polar phase having a small pore size) column was also tried, but the two major products (acetone and propionaldehyde) could not be separated. All the radiolysis products were identified by their retention times on silica gel and Carbowax-20M.

## F. Computer Simulation

A computer program designed to deal with steady state kinetics was used to test the validity of the proposed mechanisms. The computer simulation program was originally written in FORTRAN II by DeTar (67) and was modified to FORTRAN IV and used on an S-100 bus CP/M based Z80 microcomputer. The FORTRAN IV version of the program has been included in Appendix IV.

The program was modified to create a disk file of the predicted concentration versus time data, as well as printing it on the console video display or line printer. The output data file was picked up from the disk by a BASIC program which normalized the concentration data and displayed the data in graphical form on the video screen using a Vector Graphics high-resolution bit-mapped graphics board on an Integral Data System Model 225 dot-matrix printer using special assembly language subroutines.

The input parameters to the DeTar program are the mechanistic steps, their rate constants, the identification of reactants and products, the initial concentrations and the information which controls the computational intervals. The program furnishes the concentration of each chemical species as a function of time. The algorithm used to perform the calculations is trapezoidal integration of the set of simultaneous rate equations.

## III. THE GAMMA RADIOLYSIS OF PROPANE

### A. Experimental Results

The nickel vessels were filled with 100 torr of propane gas and irradiations were carried out at 25 °C in a Co-60 gamma source over an absorbed dose range of 1.55 x $10^{20}$-1.40x$10^{21}$ eV $g^{-1}$. The dose rate in propane was found to be 1.94x$10^{19}$ eV $g^{-1}h^{-1}$. Each sample contained approximately 0.026 g $C_3H_8$.

Figure 11 shows a typical chromatogram of the non-condensible products and Figure 12 shows the chromatogram of the condensible organic products. In all 12 products were identified by their retention times. Figures 13 to 18 show the yields of major and minor products as a function of dose. These yields are linear with absorbed dose. The major products are hydrogen, methane, ethane, iso-butane, n-butane, iso-pentane, n-pentane, and hexanes while the minor products are heptanes, octanes, nonanes and decanes. Small yields of ethylene and propylene were also observed. The G-values of various products along with the results of earlier investigators are listed in Table 1.

The G-values in the presence of 10% oxygen are listed in Table 2, along with the values reported by Yang and

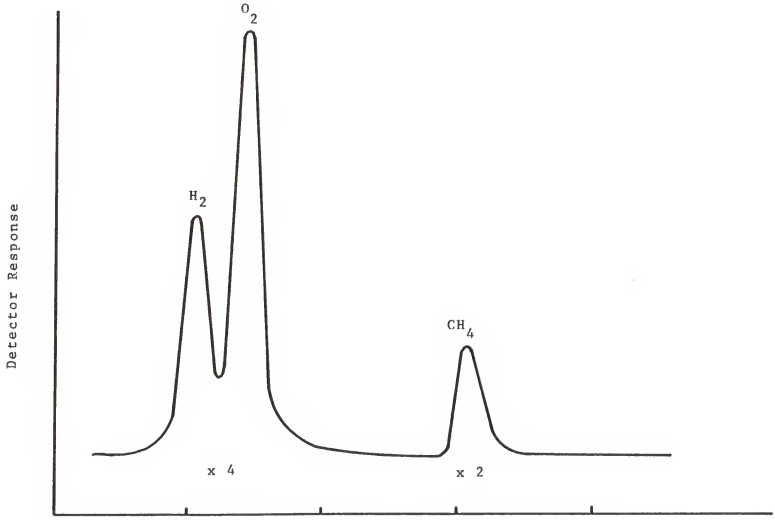



Fig. 11 Gas chromatogram of the noncondensible products in the radiolysis of propane.

Fig. 12 Gas chromatogram of irradiated propane

Peak Identification

1. Methane
2. Ethane
3. Propane
4. Iso-Butane
5. N-Butane
6. Iso-Pentane
7. N-Pentane
8. Hexanes
9. Heptanes
10. Octanes
11. Nonanes
12. Decanes

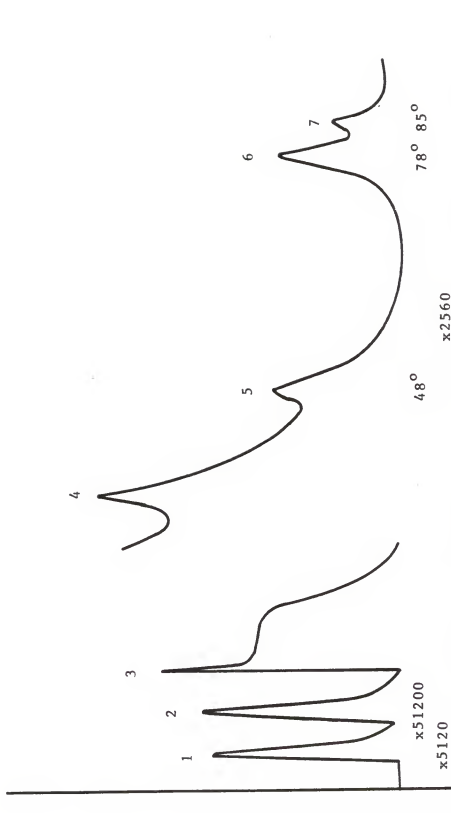



Fig. 12a Gas chromatogram of irradiated propane.

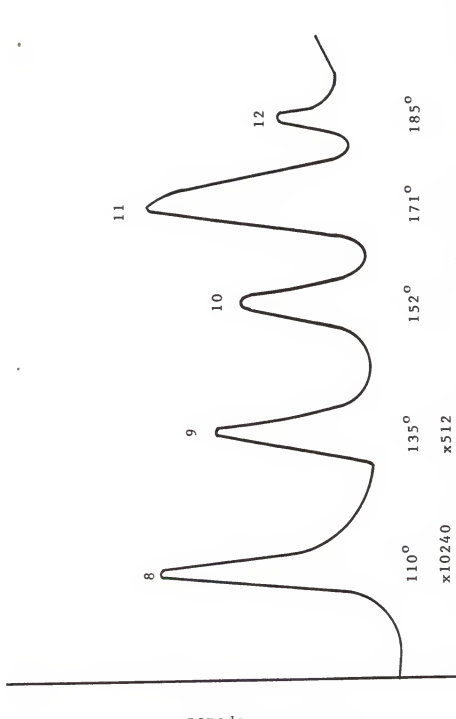



Fig. 12b Gas chromatogram of irradiated propane.

Table 1

A Comparison of the G-Values for the Radiolysis Products from Propane

| Type of Radiation | Gamma | Gamma | Gamma | Alpha | Electrons |
|---|---|---|---|---|---|
| Pressure, cm Hg | 10 | 388 | 60 | 76 | 4.0 |
| Temperature, °C | 25 | 20-25 | 25 | 25 | 25 |
| Product | This Work | Birdwell & Crawford (1) | Yang & Manno (4) | Lind & Bardwell (5) | Bone, Blocker & Futrell (15) |
| Hydrogen | 4.99 | (5.9)[d] | 5.9 | (5.9)[d] | ---- |
| Methane | 1.30 | 1.59 | 1.48 | 1.59 | 1.33 |
| Ethylene | trace | trace | 0.24 | ---- | 1.13 |
| Ethane | 1.95 | 1.89 | 2.01 | 0.94 | 1.95 |
| Propylene | trace | trace | 0.24 | ---- | 1.95 |
| Butanes | 0.86[a] | 1.00 | 0.89 | 1.12 | 0.98 |
| Pentanes | 0.56[b] | 0.47 | 0.41 | 0.83 | 0.21 |
| Hexanes | 0.89[c] | 4.13 | ---- | ---- | 1.37 |
| Heptanes | 0.082 | ---- | ---- | ---- | ---- |
| Octanes | 0.067 | ---- | ---- | ---- | ---- |
| Nonanes | 0.088 | ---- | ---- | ---- | ---- |
| Decanes | 0.033 | ---- | ---- | ---- | ---- |

a. Consisting of iso-butane, G = 0.61 and n-butane, G = 0.25
b. Consisting of iso-pentane, G = 0.42 and n-pentane, G = 0.14
c. 2,3 dimethyl butane and 2 methyl pentane
d. G-Values based on the assumption that $G(H_2) = 5.9$

Table 2

G-Value for the Radiolysis Products from Propane with Added Scavenger.

| Products | This Work 10% O2 | Yang and Manno 5% NO. |
|---|---|---|
| Hydrogen | 1.87 | 2.48 |
| Methane | 0.82 | 0.94 |
| Ethane | 1.22 | 1.36 |
| Butanes | 0.00 | 0.12 |

Table 3

Per Cent Free Radical Contribution

| Products | This Work | Yang and Manno |
|---|---|---|
| Hydrogen | 63 | 58 |
| Methane | 37 | 36 |
| Ethane | 17 | 32 |
| Butanes | 100 | 87 |

Table 4

G-Values of Products at Different Oxygen Concentrations of Oxygen in the Gamma Radiolysis of Propane

| Products | Amount of Added Oxygen | | | | | |
|---|---|---|---|---|---|---|
| | 0% | 0.7% | 2% | 5% | 10% | 15% |
| Hydrogen | 4.99 | 3.25 | 2.30 | 1.90 | 1.87 | 1.86 |
| Methane | 1.30 | 1.12 | 0.94 | 0.88 | 0.82 | 0.82 |
| Ethane | 1.95 | 1.32 | 1.28 | 1.27 | 1.22 | 1.23 |

Table 5

Mechanism Used for Computer Simulation
of Radiolysis of Propane

| | Process | G-value/Rate constant | Reference |
|---|---|---|---|
| S1. | $C_3H_8 \sim\sim\sim\

Table 5 (continued)

| | Process | G-value/Rate constant | Reference |
|---|---|---|---|
| S14. | $CH_3^{\bullet} + CH_3^{\bullet} \longrightarrow C_2H_6$ | k = 2.5 E10 | (68,70) |
| S15. | $C_2H_5^{\bullet} + C_2H_5^{\bullet} \longrightarrow C_2H_6 + C_2H_4$ | k = 1.0 E10 | (71) |
| S16. | $C_2H_5^{\bullet} + C_2H_5^{\bullet} \longrightarrow C_4H_{10}$ | k = 1.4 E10 | (71, range) |
| S17. | $CH_3^{\bullet} + C_3H_7^{\bullet} \longrightarrow C_4H_{10}$ | k = 1.2 E10 | (68) |
| S18. | $C_2H_5^{\bullet} + C_3H_7^{\bullet} \longrightarrow C_5H_{12}$ | k = 1.6 E10 | (70) |
| S19. | $C_3H_7^{\bullet} + C_3H_7^{\bullet} \longrightarrow C_6H_{14}$ | k = 3.4 E9 | (72, range) |
| S20. | $C_3H_7^{\bullet} + C_3H_7^{\bullet} \longrightarrow C_3H_6 + C_3H_8$ | k = 2.0 E9 | (70, range) |
| S21. | $C_3H_5^{\bullet} + C_3H_7^{\bullet} \longrightarrow C_3H_6 + C_3H_6$ | k = 2.0 E9 | (70) |
| S22. | $C_2H_4$ + Wall $\longrightarrow$ Polymer | k = 5.0 E-2 | arbitrary |
| S23. | $C_3H_6$ + Wall $\longrightarrow$ Polymer | k = 1.0 E-1 | arbitrary |
| S24. | $C_3H_8$ + Wall $\longrightarrow$ Polymer + $H_2$ | G = 1.79 | |

Table 6

Yields of Primary Processes in Radiolysis of Pure Propane From Computer Modeling Calculation

| Process | G-value |
|---|---|
| (1) $C_3H_8$ ------> ($C_3H_8^*$) ----> $C_2H_5^\cdot$ + $CH_3^\cdot$ | 1.00 |
| (2) $C_3H_8$ ------> $C_3H_7^\cdot$ + $H^*$ | 1.11 |
| (3) $C_3H_8$ ------> $H_2$ + $C_3H_6$ | 1.67 |
| (4) $C_3H_8$ ------> $CH_4$ + $C_2H_4$ | 0.83 |
| (5) $C_3H_8$ ------> $C_2H_5^*$ + $CH_3^\cdot$ | 1.22 |
| (6) $C_3H_8$ ------> $C_3H_5^\cdot$ + $H^\cdot$ + $H_2$ | 0.20 |
| (7) $C_3H_8$ ------> $H_2$ + Polymer | 1.79 |

Table 7

Comparison of Measured and Computed Yields in Pure Propane System

| Product | G-Measured | G-Computed |
|---|---|---|
| Hydrogen | 4.99 | 4.99 |
| Methane | 1.30 | 1.32 |
| Ethane | 1.95 | 1.96 |
| Butanes | 0.86 | 0.88 |
| Pentanes | 0.56 | 0.54 |
| Hexanes | 0.89 | 0.89 |

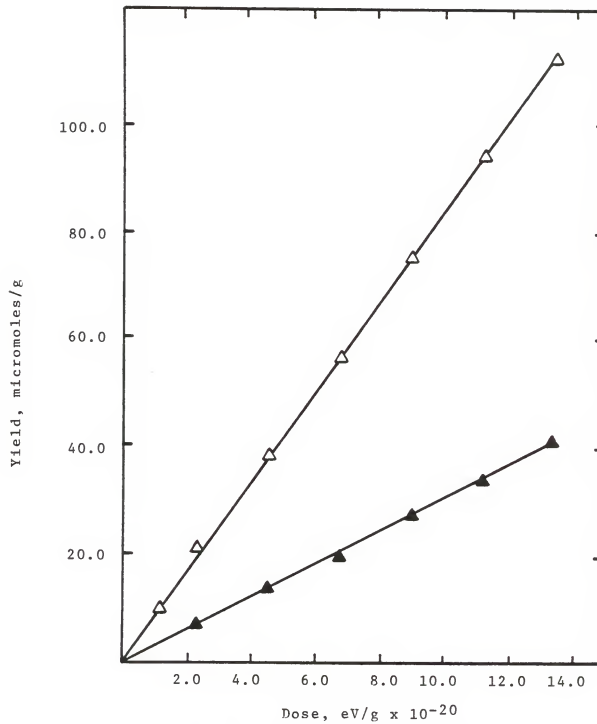



Fig. 13 Production of hydrogen (pure, △; 10% $O_2$, ▲ ) as a function of dose in propane radiolysis.

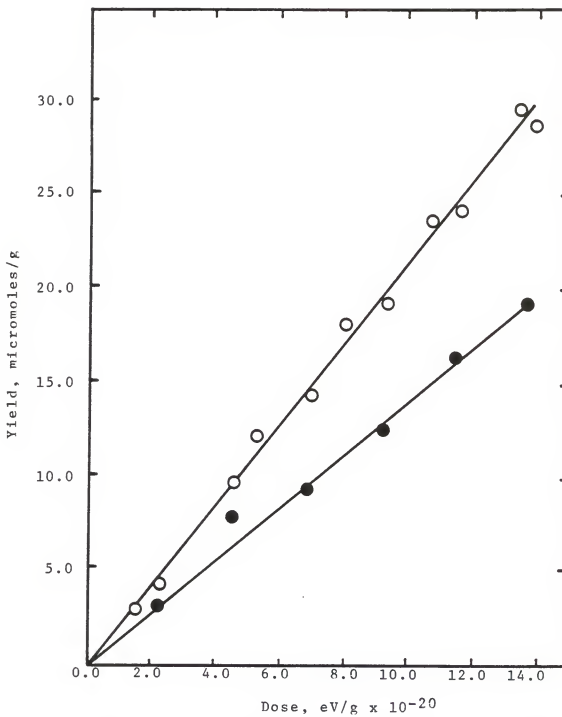



Fig. 14 Production of $CH_4$ (pure, ○ : 10% $O_2$, ●) as a function of dose in propane radiolysis.

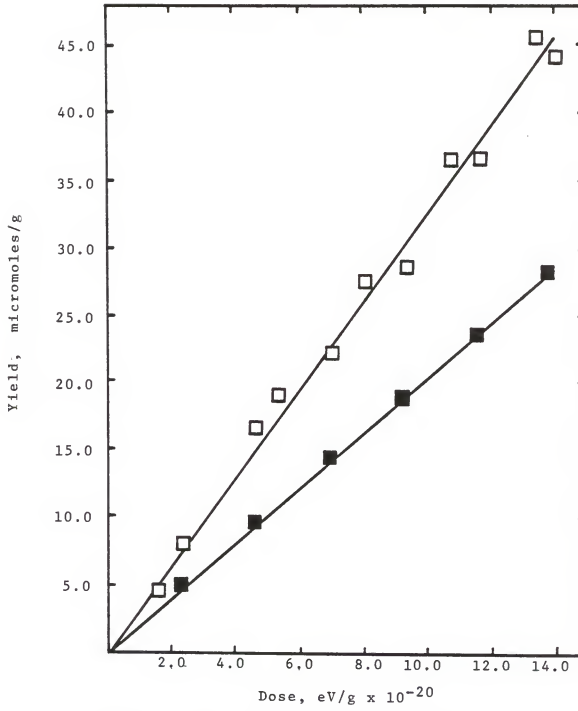



Fig. 15 Production of $C_2H_6$ (pure, □; 10% oxygen, ■ ) as a function of dose in propane radiolysis.

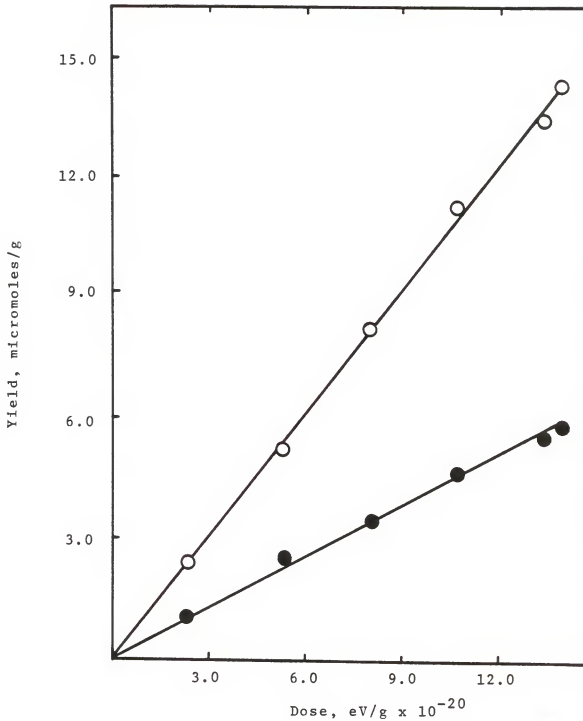



Fig. 16 Production of i-$C_4H_{10}$ ○ and n-$C_4H_{10}$ ● as a function of dose in propane radiolysis.

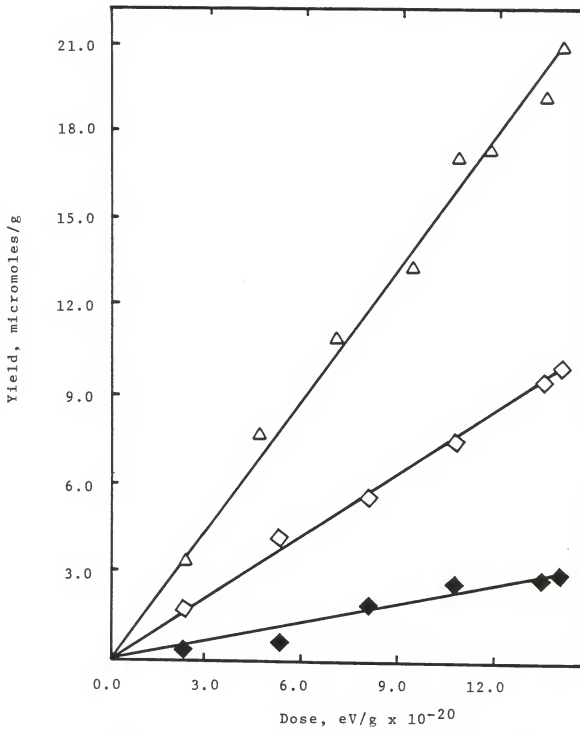



Fig. 17 Production of $C_6H_{14}$ △ ; i-$C_5H_{12}$ ◇ and n-$C_5H_{12}$ ◆ as a function of dose in propane radiolysis.

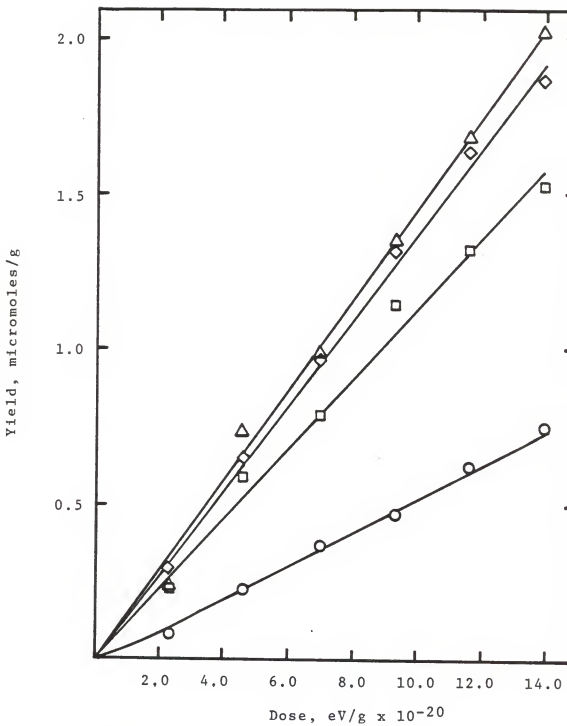



Fig. 18 Production of nonanes, △; heptanes, ◇; octanes, □ and decanes, ○ as a function of dose in propane radiolysis.

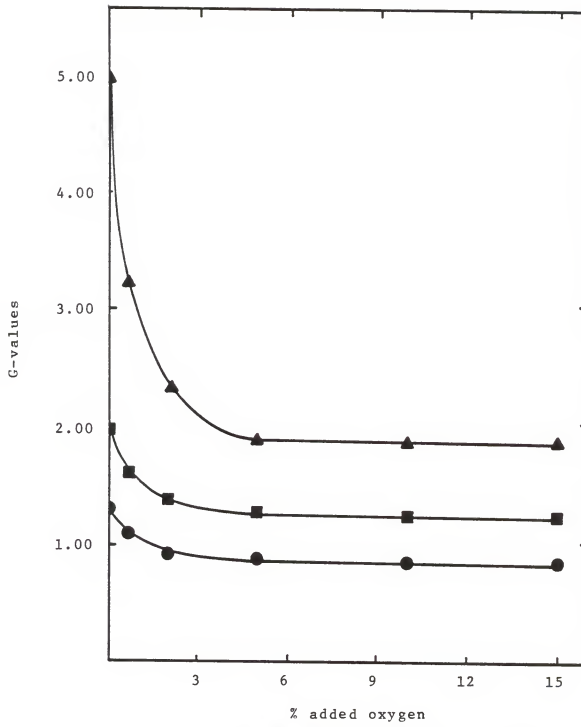



Fig. 19 G-values of hydrogen, ▲; ethane, ■ and methane, ● as a function of added oxygen in the radiolysis of propane.

Manno (4) in the presence of 5% NO. When oxygen is added as a scavenger to propane, it was found that the yield of hydrogen was reduced by 63%, methane by 37% and ethane by 37%. This is shown in Table 3. All the higher saturated hydrocarbons such as butanes, pentanes, hexanes, octanes, nonanes and decanes were eliminated. Figure 19 shows the variation of the values of hydrogen methane and ethane as a function of percent added oxygen.

## B. Discussion

Previous reports of the product yield in gas phase propane radiolysis show considerable disagreement in the results. This is seen in Table 1, where the results of this work are compared to the work of other investigators (1,4,5,15). In most reported investigations the material balance is not particularly good with a hydrogen to carbon ratio of 2.96 for the work of Bone, Sieck, and Futrell (20), 2.82 for Birdwell and Crawford (5), 3.74 for Yang and Manno (4), 3.71 for Lind and Bardwell (1) and 3.14 for this work.

The effect of scavenger on the radiolysis of propane was previously reported by Yang and Manno; they used NO as a scavenger whereas $O_2$ was employed in the present work. In the presence of oxygen, the hydrogen yield decreased by 63% and the yields of methane and ethane were reduced by

37%. All the higher saturated hydrocarbons were eliminated, indicating that these products were formed from radicals. From the results obtained it is possible to propose a reaction scheme for the formation of major products through $C_6$.

When a gas is irradiated, both excited and ionized molecules are formed (Reaction 1a,1b). The excited propane can decompose to give molecular hydrogen and propylene, methane and ethylene, ethane and methylene, propyl radical and hydrogen atom, and an ethyl radical and a methyl radical. Reactions 2 to 6 are well established through photochemical studies (20,34,73).

$$C_3H_8 \text{ ~~~~~> } C_3H_8^* \quad (1a)$$

$$C_3H_8 \text{ ~~~~~> } C_3H_8^+ + e^- \quad (1b)$$

$$C_3H_8^* \text{ ----> } H_2 + C_3H_6 \quad (2)$$

$$C_3H_8^* \text{ ----> } CH_4 + C_2H_4 \quad (3)$$

$$C_3H_8^* \text{ ----> } C_2H_6 + CH_2 \quad (4)$$

$$C_3H_8^* \text{ ----> } C_3H_7^\bullet + H^\bullet \quad (5)$$

$$C_3H_8^* \text{ ----> } C_2H_5^\bullet + CH_3^\bullet \quad (6)$$

Reactions 2, 3, and 4 account for non-scavengable yields of $H_2$, $CH_4$, $C_2H_6$.

The radicals react by combination, disproportionation or abstraction from substrate to give various products. Iso and normal products are formed depending on whether $i\text{-}C_3H_7^\bullet$ or $n\text{-}C_3H_7^\bullet$ takes part in the reaction. Reactions 7, 8, 9,

11, 13, and 14 have been proposed by Steacie and Dewar (73). Reactions 10 and 12 have been proposed by Okabe and McNesby (34).

Abstraction:

$$H^{\cdot} + C_3H_8 \longrightarrow H_2 + C_3H_7^{\cdot} \quad (7)$$

$$CH_3^{\cdot} + C_3H_8 \longrightarrow CH_4 + C_3H_7^{\cdot} \quad (8)$$

$$C_2H_5^{\cdot} + C_3H_8 \longrightarrow C_2H_6 + C_3H_7^{\cdot} \quad (9)$$

Combination:

$$CH_3^{\cdot} + CH_3^{\cdot} \longrightarrow C_2H_6 \quad (10)$$

$$C_2H_5^{\cdot} + C_2H_5^{\cdot} \longrightarrow C_4H_{10} \quad (11)$$

$$CH_3^{\cdot} + C_3H_7^{\cdot} \longrightarrow C_4H_{10} \quad (12)$$

$$C_2H_5^{\cdot} + C_3H_7^{\cdot} \longrightarrow C_5H_{12} \quad (13)$$

$$C_3H_7^{\cdot} + C_3H_7^{\cdot} \longrightarrow C_6H_{14} \quad (14)$$

Disproportionation:

$$CH_3^{\cdot} + C_3H_7^{\cdot} \longrightarrow CH_4 + C_3H_6 \quad (15)$$

$$C_2H_5^{\cdot} + C_2H_5^{\cdot} \longrightarrow C_2H_6 + C_2H_4 \quad (16)$$

$$C_2H_5^{\cdot} + C_3H_7^{\cdot} \longrightarrow C_2H_4 + C_3H_8 \quad (17)$$

$$C_2H_5^{\cdot} + C_3H_7^{\cdot} \longrightarrow C_2H_6 + C_3H_6 \quad (18)$$

$$C_3H_7^{\cdot} + C_3H_7^{\cdot} \longrightarrow C_3H_6 + C_3H_8 \quad (19)$$

$$C_3H_5^{\cdot} + C_2H_5^{\cdot} \longrightarrow C_3H_6 + C_2H_4 \quad (20)$$

$$C_3H_5^{\cdot} + C_3H_7^{\cdot} \longrightarrow C_3H_6 + C_3H_6 \quad (21)$$

When oxygen is added as a scavenger it is seen that the yields of hydrogen, methane and ethane are decreased, which means that there is a radical yield of the products.

Products containing 4 or more carbon atoms are eliminated in the presence of oxygen indicating that they are all formed by radical reactions. Reactions 7-21 account for the scavengable yields of $H_2$, $CH_4$, $C_2H_6$, $C_4H_{10}$, $C_5H_{12}$, and $C_6H_{14}$.

Methylene formed in reaction 4 inserts itself into propane to form excited butane (Reaction 22), which undergoes decomposition to give methyl and propyl radicals, and two ethyl radicals (Reaction 23, 24).

$$CH_2 + C_3H_8 \longrightarrow C_4H_{10}^* \quad (22)$$

$$C_4H_{10}^* \longrightarrow CH_3^\bullet + C_3H_7^\bullet \quad (23)$$

$$C_4H_{10}^* \longrightarrow 2C_2H_5^\bullet \quad (24)$$

Products containing 7 or more carbon atoms are formed as follows:

$$R^\bullet + A \longrightarrow RA^\bullet$$

$$2RA^\bullet \longrightarrow (RA)_2$$

$$R^\bullet + RA^\bullet \longrightarrow RAR$$

where $R^\bullet$ is a radical and A is an alkene $C_2H_4$ or $C_3H_6$.

Along with the radical/excited molecular reaction scheme described above, numerous ionic processes also occur, following primary ionization (Reaction 1b). These

processes contribute substantially to certain product yields. A sequence of elementary reactions has been demonstrated by Bone and Futrell which lead to $C_3H_8^+$ and $C_3H_7^+$ as stable ions (33). In the mass spectrum of propane three ions constitute over 60% of the total ionization (18); $C_2H_5^+$ (30.5%), $C_2H_4^+$ (18.1%) and $C_2H_3^+$ (12.3%)

$$C_3H_8^+ \longrightarrow C_2H_5^+ + CH_3\cdot \quad (25)$$

$$\longrightarrow C_2H_4^+ + CH_4 \quad (26)$$

$$\longrightarrow C_2H_3^+ + H_2 + CH_3\cdot \quad (27)$$

Hydrogen is also produced by the molecular elimination from $C_2H_5^+$, $C_2H_4^+$ etc (7). The various fragment ions ($C_2H_3^+$, $C_2H_4^+$, $C_2H_5^+$ etc.) take part in a series of ion-molecule reactions involving parent $C_3H_8$, which ultimately lead to only two catonic products, $C_3H_7^+$ and $C_3H_8^+$ (33); $C_3H_8^+$ and $C_3H_7^+$ ultimately undergo neutralization to give $C_3H_8^{**}$.

$$C_2H_5^+ + C_3H_8 \longrightarrow C_2H_6 + C_3H_7^+ \quad (28)$$

$$C_2H_4^+ + C_3H_8 \longrightarrow C_2H_5\cdot + C_3H_7^+ \quad (29)$$

$$\longrightarrow C_2H_6 + C_3H_6^+ \quad (30)$$

$$C_2H_3^+ + C_3H_8 \longrightarrow C_2H_4 + C_3H_7^+ \quad (31)$$

$$\longrightarrow C_3H_6 + C_2H_5^+ \quad (32)$$

$$\longrightarrow C_2H_6 + C_3H_5^+ \quad (33)$$

$$C_3H_6^+ + C_3H_8 \longrightarrow C_3H_8 + C_3H_6^+ \quad (34)$$

$$\longrightarrow C_3H_7\cdot + C_3H_7^+ \quad (35)$$

Reactions (25-35) produced portions of the yields of $H_2$, $CH_4$, and $C_2H_6$, as well as $H^{\bullet}$, $CH_3^{\bullet}$ and $C_2H_5^{\bullet}$ radicals.

Formation of Major Products

Hydrogen: Hydrogen is formed directly from the decomposition of excited propane (Reaction 2). Molecular elimination of $C_3H_8^+$, $C_2H_5^+$, $C_2H_4^+$, etc. (7) also yields hydrogen. These reactions account for the non-scavengable yield of hydrogen, the G-value of which is 1.87 in the presence of oxygen.

Hydrogen radical abstracts a hydrogen atom from the substrate to give molecular hydrogen (Reaction 7), which accounts for the scavengable yield of hydrogen. The free radical contribution for the formation of hydrogen is 63%.

Methane: Methane is formed directly by the decomposition of excited propane (Reaction 3). It is also formed from $C_3H_8^+$ (Reaction 26) (7). Reactions 3 and 26 account for the non-scavengable yield of methane, the G-value of which is 0.82 in the presence of oxygen.

Methyl radicals formed in reaction 6 abstract a hydrogen from substrate to give methane (Reaction 8) (73). A methyl and a propyl radical disproportionate to yield methane (15). These reactions 8 and 15 account for the scavengable yield of methane. The free radical contribution for the formation of methane is 37%.

Ethane: Excited propane decomposes to give ethane (Reaction 4). It is also formed by the ion-molecule reaction of $C_2H_5^+$, $C_2H_4^+$ and $C_2H_3^+$ with $C_3H_8$ (Reaction 28, 30, and 33). This accounts for the non-scavangable yield of ethane, the G-value of which is 1.22 is the presence of oxygen.

The ethyl radical formed in reaction 6 abstracts a hydrogen atom from the substrate to give ethane (Reaction 9) (73). Two methyl radicals recombine and form ethane (Reaction 10) (34). Two ethyl radicals disproportionate to give ethane and ethylene (Reaction 16). An ethyl radical and a propyl radical can disproportionate to give ethane and propylene (Reaction 18). All these reactions 6, 9, 10, 16, and 18 account for the scavengable yield of ethane. The free radical contribution for the formation of ethane is 37%.

Butanes: Butanes are formed in two ways:
(a) Recombination of two ethyl radicals (Reaction 11).
(b) Combination of a methyl and a propyl radical (Reaction 12).

Pentanes: Pentanes are formed by the combination of ethyl and propyl radicals (Reaction 13).

Hexanes: Hexanes are formed by the recombination of two propyl radicals (Reaction 14).

Since radicals are scavanged by oxygen, and butanes, pentanes and hexanes are not observed in the presence of oxygen, the $C_4$, $C_5$, and $C_6$ products are formed by free radical reactions (Reactions 11, 12, 13, and 14).

Computer Simulation of the Radiolysis Mechanism

A major goal of the present work was to carry out computer modeling of the reaction kinetics, in order to investigate the internal consistency of the yield data, as well as the adequacy of a simple reaction scheme to describe the data. The mechanism consisting of reactions given in Table 5 was tested using rate constants given in the literature. Since the entire scheme is too complex to be suitable for modeling, several simplifications were made in selecting a subset for the computer work. In particular, it was assumed that ion-molecule processes were completed before onset of the secondary radical reaction stage, and that the ionic processes in effect constitute additional pathways to the same set of primary products and radical intermediates as formed via neutral fragmentation and elimination reactions. (It was necessary to account explicitly for the role of $C_2H_5^+$ in the mechanism, as explained below.)

Formation of $C_1$ and $C_2$ radicals is represented as occurring via a two step sequence (Reaction S1 and S7 in Table 5) due to the observation that essentially no oxygen containing $C_1$ and $C_2$ products are observed in the presence of added oxygen. The species designated $C_2H_5^{\#}$ in step 5 is in fact known to be $C_2H_5^+$ ion, which is a precursor to a (nearly) unscavengable $C_2H_6$ yield via an $H^-$ transfer process. Reaction S8 is a simplified representation of this process; it ignores charge state and the problem of ion-neutralization. It is thus assumed that the $C_3H_7^+$ ion actually formed in Reaction S8 is a precursor to $C_3H_7^{\bullet}$ radical via an unspecified reaction path. Reaction S6 has been added to the scheme, because allyl radical plays an important role in the radiolytic oxidation of propane, in the formation of allyl alcohol and acraldehyde.

Reactions S1-S6 were assigned pseudo-rate constants on the bases of the G values given in Table 5. That is, the G value was converted to an actual rate of product formation in units of moles, liters, and seconds, using the known dose rate in the system.

The apparent first order rate constants ($k_{Pseudo}$) for the primary reactions are calculated as follows:

$$G = \frac{\text{(Molecules/sec) x 1Ø0}}{\text{(eV deposited/liter sec)}}$$

$$\text{Molecules/sec} = \frac{G \times (\text{eV/liter sec})}{100}$$

$$\frac{\text{Moles}}{\text{liter sec}} = \frac{G \times (\text{eV/liter sec})}{100 \times N_o}$$

$$\text{Let } Y = \frac{\text{Moles}}{\text{liter sec}} = \text{Rate} = K_{\text{Pseudo}} [C_3H_8]$$

$$k_{\text{Pseudo}} = \frac{Y}{[C_3H_8]} = \frac{\text{Rate}}{[C_3H_8]}$$

If the approximate G-value is known, Y which is in moles/(liter sec) can be calculated; and knowing the concentration of $C_3H_8$ in moles/lit, $k_{pseudo}$ can be calculated.

This procedure was required since the kinetic integrator package can handle only first or second order processes. Since the propane concentration is virtually constant, the procedure described leads to a constant rate of formation of the species in question. (Third order processes usually involve the substrate as a third body; they are conveniently treated as second order by multiplying the third body concentration into the termolecular rate constant, giving an effective bimolecular rate constant.)

The rate constant for Reaction S7 was given the value of $9.0 \times 10^{7}$ sec$^{-1}$ in the present study, since further work on oxygen-containing products suggested that this reaction may be subject to interference (via collisional deactivation of $C_3H_8^*$) at high concentrations of added $O_2$. This process will be the exclusive fate of $C_3H_8^*$ in the unscavenged system, since no competitive fate of the reactant is indicated. The radical products would presumably be trapped with any substantial concentration of added oxygen. Reaction S8 was assigned an appropriate high rate constant for an efficient ion-molecule reaction, and Reactions S9 and S10 were given arbitrary rate constants of $1 \times 10^{9}$ liter mole$^{-1}$ sec$^{-1}$. Rate constants in this range permit interference by oxygen in the 1 to 15% concentration range, as observed in the radiolytic oxidation of propane.

Reactions S11 to S21 were, in general, assigned the best available values obtained from the literature (68-72). There was a problem in the case of reaction S16, however, since published rate constants varied over a wide range from $2.24 \times 10^{9}$ liter mole$^{-1}$ sec$^{-1}$ to $6.6 \times 10^{10}$ liter mole$^{-1}$ sec$^{-1}$; we used an intermediate values of $1.4 \times 10^{10}$. Reaction S19 has published values which vary from $3.16 \times 10^{6}$ to $6.31 \times 10^{9}$ liter mole$^{-1}$ sec$^{-1}$. We tried several values which lie in the range of $1.59 \times 10^{9}$ liter mole$^{-1}$ sec$^{-1}$ to $6.31 \times 10^{9}$ liter mole$^{-1}$ sec$^{-1}$ (72); the value used in computing the curves in Figure 20 and 21 was $3.4 \times 10^{9}$ liter mole$^{-1}$ sec$^{-1}$.

We also assigned arbitrary values of $1x10^{2}$ to Reactions S12 and S13 because the literature values (28 and 1.48 liter $mole^{-1}$ $sec^{-1}$) appeared implausibly small. In fact, use of these literature values gave computed yield curves in clear disagreement with the experimental results of the present work.

The input to the computer program was, essentially, the yields of molecular hydrocarbon products from the oxygen scavenged system plus the set of thermal radical Reactions S12-S21, along with their rate constants. Yields for two primary processes leading to radical intermediates (Reaction S1 and S2) were varied to achieve the best fit of product yields in the absence of scavenger. About 100 computer runs were carried out. The yields for the primary processes used in the best-fit computer calculations are given in Table 6. Table 7 shows a comparison of measured and computed yields of the products. Figures 20 and 21 show the plot of concentration versus time of the various products obtained by computer simulation. A print out of the mechanism, their rate constants, concentration of products at various time periods and the data sheet are given in Appendix V.

Although for processes S7-S10 rate constants are listed as "arbitrary" in Table 5, these parameters are not "degrees of freedom," subject to adjustment for improvement of the predicted results. The reason is that Reactions S7,

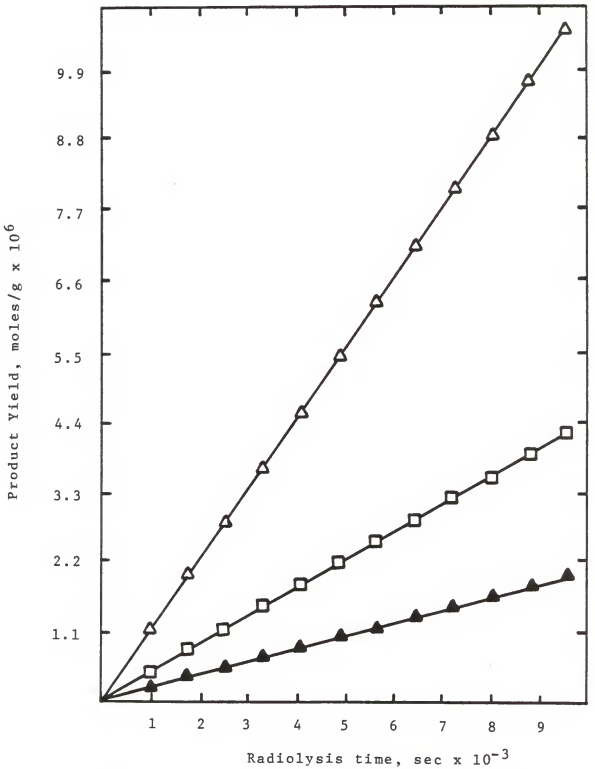



Fig. 20 Computer predicted yields of hydrogen, △; ethane, □ and hexanes, ▲ as a function of radiolysis time.

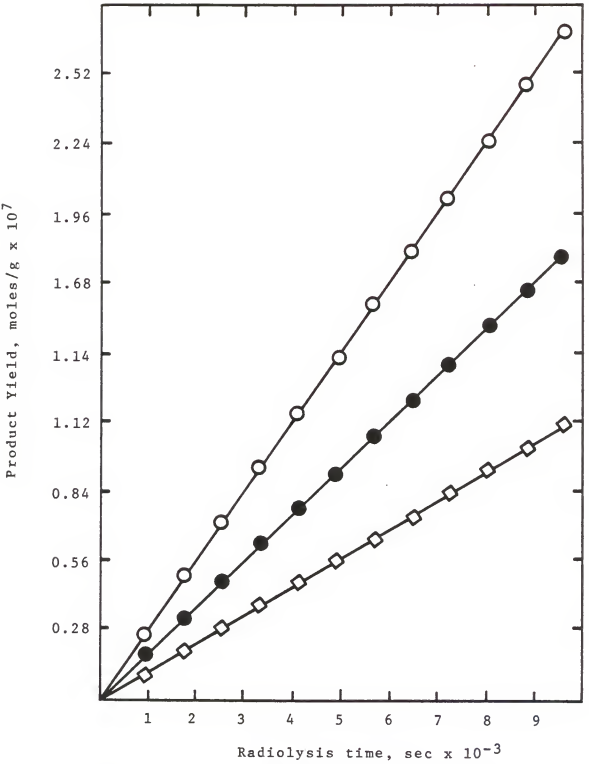



Fig. 21 Computer predicted yields of methane, ○; butanes, ● and pentanes, ◇ as a function of radiolysis time.

S8, and the pair S9-S1Ø are the only reaction channels specified for $C_3H_8^*$, $C_2H_5^\#$, and $H^*$ respectively. The only adjustment which would affect predictions is the ratio kS9/kS1Ø. Since yields of five products (excluding hydrogen) were predicted with only two entirely free variables ($G_{S1}$ and $G_{S2}$), it is clear that the computer integration computation not only tests consistency between the reaction scheme and the predicted yields, but also has at least some predictive value. (There was some adjustment made to other rate conatants, as mentioned previously.)

The situation regarding the hydrogen yield requires separate discussion. In this study and essentially in all other investigations of the gas phase radiolysis of saturated hydrocarbons, there is a material balance problem, in that the hydrogen yield is considerably in excess of the combined yields of unsaturated and telomeric hydrocarbons needed to account for it on the basis of stoichiometry.

This problem has been disposed of arbitrarily in the modeling calculations by postulating the deposition of olefins on the vessel walls (presumably as polymer). Although arbitrary, this assumption may well be essentially correct, since strong heating of the radiolysis vessels after removal of volatile products usually produces considerable outgassing, presumably of pyrolysis products.

An essentially similar postulate was presented earlier by Bone, Sieck, and Futrell (19), who concluded that a substantial part of the hydrogen yield arises from neutralization of the "unreactive" ion $C_3H_7^+$ at the vessel walls. They did not discuss in detail what becomes of the residual hydrocarbon moieties, but it appears that most of it ends up as polymer on the walls, on the basis of the material balance situation.

As mentioned above, the ionic processes implied by but not explicitly included in our reaction scheme have been discussed in detail elsewhere (19,29-33). It is also known, particularly from the work of Ausloos and coworkers, that there is an additional neutral fragmentation process which we did not include

$$C_3H_8 \dashrightarrow C_2H_6 + CH_2$$

The ethane formed is a part of the "molecular" yield and the carbene inserts into substrate, giving a "hot" butane which can be stabilized or fragmented into two ethyl radicals or a methyl plus a propyl radical. Some computations were performed including these steps, but ultimately it was decided to omit them for the practical reason that the complexity of the scheme was beginning to tax the capabilities of the relatively simple kinetic integrator. For the same reason, no distinction was made between n-propyl and i-propyl radicals in the radiolysis of pure

propane. (The latter distinction came to be of major importance in the oxygen-containing products in the radiolytic oxidation of propane, since i-propyl radical is precursor to i-propyl alcohol and acetone, whereas n-propyl radical forms n-propyl alcohol and propionaldehyde.)

Effectively, the kinetic integrations performed in the computation scheme concern reactions occurring on the $10^{-6}$ to $10^{-3}$ s time scale, integrated over minutes to hours. In principle, it would be feasible to carry out computations on the $10^{-12}$ to $10^{-6}$ s time scale, which would use mass spectrometric fragmentation patterns and W values as input data (along with information from VUV photochemistry for the neutral processes) in conjunction with ion-molecule reaction rate data. An attempt to do this was not made, mainly because most of the ion-molecule reaction work on propane was done in the rather qualitative 1960 - 1965 era; for the most part, reaction pathways were identified, but rate constants (or cross sections) were not measured.

## C. Summary

The gamma-radiolysis of gaseous propane was studied at 100 torr pressure and 25 °C, both pure and with 10% added oxygen. For the pure system, the major radiolytic products and their respective G-values were hydrogen, 4.99; methane,

1.30; ethane, 1.95; i-butane, 0.61; n-butane, 0.25; i-pentane, 0.42; n-pentane, 0.14 and hexane, 0.89. The minor products included heptanes, octanes, nonanes and decanes. Small yields of ethylene and propylene were also observed. Several of the higher products had not been reported previously. It was observed that the addition of 10% oxygen reduced the hydrogen yield by 63%, methane by 37% and ethane by 37%. All higher saturated hydrocarbons were eliminated in the presence of oxygen. The results were discussed in terms of both excited and ionized propane. In the mass spectrum of propane three ions constitute over 60% of the total ionization, $C_2H_5^+$(30.5%), $C_2H_4^+$ (18.1%) and $C_2H_3^+$ (12.3%). The fragment ions then undergo ion molecule reaction with propane which contribute substantially to certain product yields. The non-scavengable products were accounted for primarily by the direct interaction of propane with gamma rays to give molecular products and by various ion-molecule reactions. The scavangable products were attributed to the radical fragments, which react by combination, disproportionation or abstraction from the substrate. The reaction scheme for the formation of major products through $C_6$ was examined using computer modeling based on a mechanism involving 24 reactions and their rate constants. Yields could be brought into agreement with the data within experimental error in nearly all the cases, but

it was necessary to assume that the molecular hydrogen yield was accompanied by the deposition of polymer on the vessel walls.

## IV. RADIOLYTIC OXIDATION OF PROPANE

### A. Experimental Results

At the onset of research there was no preconceived idea what type of oxygenated products would be formed in the radiolytic oxidation of propane; therefore a wide range of standards, which included oxygenated hydrocarbons such as ketones, aldehydes, alcohols, acids, esters, ethers, etc. were injected into the gas-chromatograph. Carbowax-20M and Porapak Q columns were used with a nitrogen carrier gas flow rate of 40 ml/min. The temperature of the oven was initially set at 60 °C for Carbowax-20M and at 80 °C for Porapak Q. Programming was started 10 minutes or 20 minutes after injection, for Porapak Q and Carbowax-20M, respectively. This procedure gave the best separation of compounds. Retention times and retention temperatures for various standards were noted as given in Table 8.

After the propane-oxygen mixtures were irradiated for different time periods, the products were transferred to a sample loop on the vacuum line; the sample loop was then attached to the gas-chromatograph for analysis. The products were identified by comparing their retention time and retention temperatures with the standards. The products

identified in the radiolytic oxidation of propane (indicated by asterisks in Table 8) were mainly ketones, aldehydes, and alcohols, which were similar to the products formed in the autoxidation of hydrocarbons. Intially both the above mentioned columns were used in the identification of products, but only the Carbowax-20M column was used for the quantitative determination of products because acetone and propionaldehyde (which were major products) were separable on Carbowax-20M but not on Porapak Q. Figure 22 a and b show a chromatogram of the condensible organic products.

The nickel vessels were filled with a mixture of propane (100 torr) and oxygen (10 torr) and irradiations were carried out at 26 $^{o}$C in a Co-60 gamma source over an absorbed dose range of $2.5 \times 10^{20}$- $15.22 \times 10^{20}$ eV/g. The dose rate was found to be $2.11 \times 10^{19}$ eV/gh. Each sample contained approximately 0.028 g of mixture (propane and oxygen).

In all 11 oxygen containing products were idenfied by their retention time and temperatures. Figures 23-27 show the yields of major and minor products as a function of dose, these yields are linear with absorbed dose. The major products are acetone, iso-propyl alcohol, propionaldehyde, acraldehyde, n-propyl alcohol and allyl alcohol, while the minor products are iso-butyl alcohol, tert-amyl alcohol, n-butyl alcohol, iso-amyl alcohol, and n-amyl

Fig. 22 Gas chromatogram of irradiated propane-oxygen mixture

Peak Identification

1. Propane
2. Propionaldehyde
3. Acetone
4. Acraldehyde
5. Iso-Propyl Alcohol
6. Tert-Amyl Alcohol
7. N-Propyl Alcohol
8. Iso-Butyl Alcohol
9. Allyl Alcohol
10. N-Butyl Alcohol
11. Iso-Amyl Alcohol
12. N-Amyl Alcohol
13. Iso-Hexyl Alcohol
14. N-Hexyl Alcohol

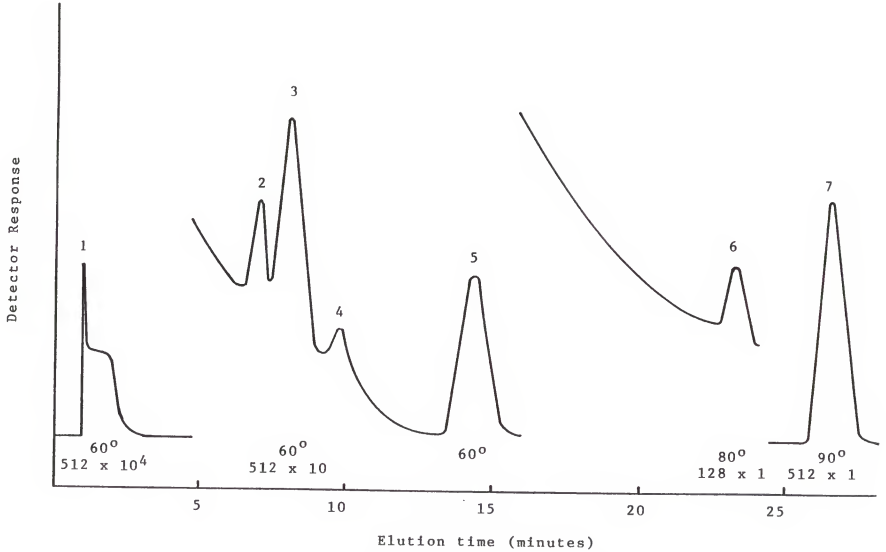



Fig. 22a Gas chromatogram of the products in the radiolytic oxidation of propane.

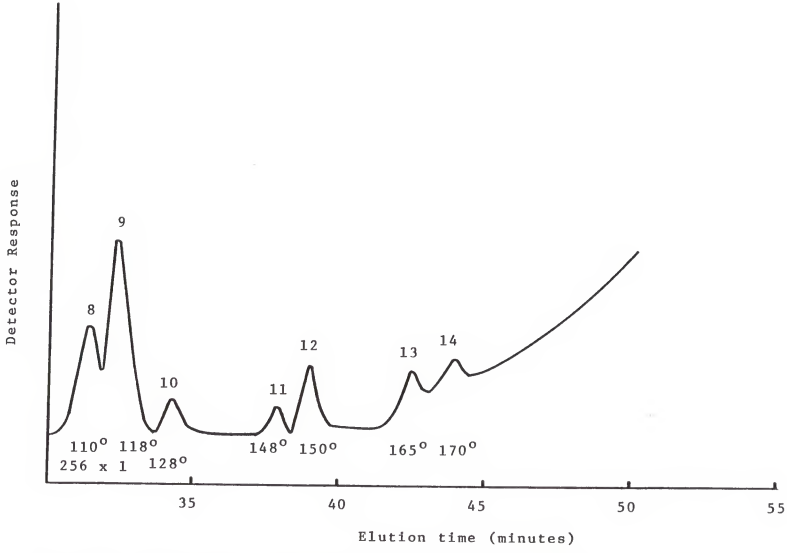



Fig. 22b Gas chromatogram of the products in the radiolytic oxidation of propane.

Table 8

Retention Times and Retention Temperatures for Various Standards

| Column | Carbowax-20M | | Porapak Q | |
|---|---|---|---|---|
| Compound | Retention Time, min | Retention Temp., °C | Retention Time, min | Retention Temp., °C |
| Formaldehyde | 3.25 | 60 | 9.14 | 80 |
| Acetaldehyde | 4.30 | 60 | 12.51 | 115 |
| Propionaldehyde* | 7.10 | 60 | 20.40 | 132 |
| I-Butyraldehyde | 10.50 | 60 | 26.10 | 158 |
| n-Butyraldehyde | 12.15 | 60 | 27.45 | 162 |
| n-Valeraldehyde | 21.45 | 60 | 32.20 | 193 |
| Acraldehyde* | 10.20 | 60 | 19.00 | 128 |
| Acetone* | 8.25 | 60 | 20.40 | 132 |
| Methyl-Ethyl ketone | 12.50 | 60 | 27.45 | 162 |
| Methanol | 13.20 | 60 | 9.35 | 80 |
| Ethanol | 15.30 | 60 | 16.50 | 115 |
| I-Propyl Alcohol* | 14.30 | 60 | 21.45 | 135 |
| N-Propyl Alcohol* | 26.45 | 90 | 24.15 | 149 |
| Sec-Butyl Alcohol | 26.00 | 89 | 23.30 | 146 |
| I-Butyl Alcohol* | 31.05 | 110 | 29.25 | 172 |
| N-Butyl Alcohol* | 34.30 | 128 | 30.40 | 180 |
| Tert-Amyl* Alcohol | 24.45 | 80 | 34.00 | 198 |

Table 8 (continued)

| Column | Carbowax-20M | | Porapak Q | |
|---|---|---|---|---|
| Compound | Retention Time,min | Retention Temp., °C | Retention Time, min | Retention Temp., °C |
| I-Amyl Alcohol* | 39.30 | 148 | 35.30 | 202 |
| N-Amyl Alcohol* | 40.10 | 148 | 36.55 | 210 |
| I-Hexyl Alcohol* | 43.05 | 165 | 38.25 | 210 |
| N-Hexyl Alcohol* | 44.00 | 170 | 42.00 | 210 |
| Allyl Alcohol* | 32.40 | 118 | 24.51 | 151 |
| Propylene oxide | 6.25 | 60 | 19.50 | 130 |
| Formic Acid | 39.40 | 149 | 17.55 | 120 |
| Acetic Acid | 46.00 | 180 | 23.30 | 145 |
| Propionic Acid | 49.00 | 193 | 30.00 | 176 |
| Methyl Acetate | 9.15 | 60 | 23.30 | 145 |
| Ethyl Acetate | 12.55 | 60 | 28.30 | 167 |
| I-Propyl Acetate | 14.00 | 60 | 32.10 | 190 |
| N-Propyl Acetate | 21.50 | 70 | 34.00 | 198 |
| N-Butyl Acetate | 30.45 | 110 | | |
| Ethyl Formate | 9.30 | 60 | | |
| N-propyl Formate | 15.45 | 60 | | |
| Methyl Propionate | 13.55 | 60 | | |
| Ethyl Propionate | 19.45 | 60 | | |

Table 8 (continued)

| Column | Carbowax-20M | | Porapak Q | |
|---|---|---|---|---|
| Compound | Retention Time,min | Retention Temp., °C | Retention Time, min | Retention Temp., °C |
| N-propyl Propionate | 28.45 | 100 | | |
| Di-Ethyl Ether | 3.45 | 60 | | |
| I-Propyl Ether | 4.20 | 60 | | |
| N-Propyl Ether | 4.25 | 60 | | |
| N-Butyl Ether | 19.30 | 60 | | |
| Allyl Ether | 4.25 | 60 | | |

* Identified in the radiolytic oxidation of propane.

Table 9

G-values for the Products Containing Oxygen in the Radiolytic Oxidation of Propane When 10% Oxygen Is Added

| Products | G-values |
|---|---|
| Acetone | 0.98 |
| Iso-Propyl Alcohol | 0.86 |
| Propionaldehyde | 0.43 |
| N-Propyl Alcohol | 0.11 |
| Acralaldehyde | 0.14 |
| Allyl Alcohol | 0.038 |
| Iso-Butyl Alcohol | $8.5 \times 10^{-3}$ |
| Tert-Amyl Alcohol | $7.4 \times 10^{-3}$ |
| N-Butyl Alcohol | $2.9 \times 10^{-3}$ |
| N-Amyl Alcohol | $1.6 \times 10^{-3}$ |
| Iso-Amyl Alcohol | 1.3 x 10-3 |
| Iso-Hexyl Alcohol | Trace |
| N-Hexyl Alcohol | Trace |

Table 10

Mechanism Used for Computer Simulation for the Radiolytic Oxidation of Propane

| | Process | | | | | G-value/Rate constant | Reference |
|---|---|---|---|---|---|---|---|
| 1. | $C_3H_8$ | | ~~~~~~> | $C_3H_8^*$ | | G = 1.00 | |
| 2. | $C_3H_8$ | | ~~~~~~> | $i\text{-}C_3H_7\cdot$ | + $H^*$ | G = 1.55 | |
| 3. | $C_3H_8$ | | ~~~~~~> | $n\text{-}C_3H_7\cdot$ | + $H^*$ | G = 0.47 | |
| 4. | $C_3H_8$ | | ~~~~~~> | $C_3H_5\cdot$ | + $H\cdot$ + $H_2$ | G = 0.20 | |
| 5. | $C_3H_8^*$ | | ---> | $C_1C_2$(Products) | | k = 9.0 E7 | arbitrary |
| 6. | $C_3H_8^*$ | + $O_2$ | ---> | $CH_3CH_2CHO$ | + $H_2O$ | k = 3.3 E10 | arbitrary |
| 7. | $C_3H_8^*$ | + $O_2$ | ---> | $C_3H_8$ | + $O_2$ | k = 3.0 E10 | arbitrary |
| 8. | $H^*$ | + $O_2$ | ---> | $HO_2\cdot$ | | k = 1.5 E9 | arbitrary |
| 9. | $H^*$ | + $C_3H_8$ | ---> | $H_2$ | + $i\text{-}C_3H_7\cdot$ | k = 1.0 E9 | arbitrary |
| 10. | $H^*$ | + $C_3H_8$ | ---> | $H_2$ | + $n\text{-}C_3H_7\cdot$ | k = 1.0 E8 | arbitrary |
| 11. | $H^*$ | + $C_3H_8$ | ---> | $H\cdot$ | + $C_3H_8$ | k = 1.0 E9 | arbitrary |

Table 10 (continued)

Mechanism Used for Computer Simulation for the Radiolytic Oxidation of Propane

| | Process | | | | | G-value/Rate constant | Reference |
|---|---|---|---|---|---|---|---|
| 12. | $H^{\bullet}$ | + $C_3H_8$ | ---> | $H_2$ | + $i\text{-}C_3H_7^{\bullet}$ | k = 9.0 E4 | (68,69) |
| 13. | $i\text{-}C_3H_7^{\bullet}$ | + $O_2$ | ---> | $i\text{-}C_3H_7O_2^{\bullet}$ | | k = 4.6 E10 | (71,74) |
| 14. | $n\text{-}C_3H_7^{\bullet}$ | + $O_2$ | ---> | $n\text{-}C_3H_7O_2^{\bullet}$ | | k = 2.0 E10 | (71,74 range) |
| 15. | $C_3H_5^{\bullet}$ | + $O_2$ | ---> | $C_3H_5O_2^{\bullet}$ | | k = 1.0 E10 | arbitrary |
| 16. | $H^{\bullet}$ | + $O_2$ | ---> | $HO_2^{\bullet}$ | | k = 3.0 E11 | (75 adjusted) |
| 17. | $2i\text{-}C_3H_7O_2^{\bullet}$ | | ---> | $2i\text{-}C_3H_7O^{\bullet}$ | + $O_2$ | k = 1.0 E10 | (76 range) |
| 18. | $2n\text{-}C_3H_7O_2^{\bullet}$ | | ---> | $2n\text{-}C_3H_7O^{\bullet}$ | + $O_2$ | k = 1.0 E9 | (76 range) |
| 19. | $2C_3H_5O_2^{\bullet}$ | | ---> | $2C_3H_5O^{\bullet}$ | + $O_2$ | k = 6.0 E10 | (76 range) |
| 20. | $HO_2^{\bullet}$ | + $HO_2^{\bullet}$ | ---> | $H_2O_2$ | + $O_2$ | k = 2.0 E9 | (75) |
| 21. | $i\text{-}C_3H_7O^{\bullet}$ | + $i\text{-}C_3H_7O^{\bullet}$ | ---> | $(CH_3)_2C{=}O$ | + $i\text{-}C_3H_7OH$ | k = 3.0 E10 | arbitrary |
| 22. | $i\text{-}C_3H_7O^{\bullet}$ | + $n\text{-}C_3H_7O^{\bullet}$ | ---> | $(CH_3)_2C{=}O$ | + $n\text{-}C_3H_7OH$ | k = 1.0 E9 | arbitrary |

Table 10 (continued)

Mechanism Used for Computer Simulation for the Radiolytic Oxidation of Propane

| | Process | G-value/Rate constant | Reference |
|---|---|---|---|
| 23. | $i\text{-}C_3H_7O^{\bullet} + n\text{-}C_3H_7O^{\bullet} \longrightarrow CH_3CH_2CHO + i\text{-}C_3H_7OH$ | k = 1.0 E9 | arbitrary |
| 24. | $n\text{-}C_3H_7O^{\bullet} + n\text{-}C_3H_7O^{\bullet} \longrightarrow CH_3CH_2CHO + n\text{-}C_3H_7OH$ | k = 1.8 E8 | arbitrary |
| 25. | $n\text{-}C_3H_5O^{\bullet} + n\text{-}C_3H_5O^{\bullet} \longrightarrow CH_2{=}CHCHO + CH_2{=}CHCH_2OH$ | k = 1.2 E10 | arbitrary |
| 26. | $i\text{-}C_3H_7O^{\bullet} + HO_2^{\bullet} \longrightarrow (CH_3)_2C{=}O + H_2O_2$ | k = 9.4 E8 | arbitrary |
| 27. | $n\text{-}C_3H_7O^{\bullet} + HO_2^{\bullet} \longrightarrow CH_3CH_2CHO + H_2O_2$ | k = 6.4 E8 | arbitrary |
| 28. | $C_3H_5O^{\bullet} + HO_2^{\bullet} \longrightarrow CH_3{=}CHCHO + H_2O_2$ | k = 4.0 E9 | arbitrary |

Table 11

Experimental G-Values of Products Containing Oxygen at Different Oxygen Concentration

| Products | Amount of Added Oxygen | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1% | 3% | 5% | 7% | 10% | 13% | 15% |
| Acetone | 1.20 | 1.11 | 1.07 | 1.04 | 0.98 | 0.97 | 0.92 |
| I-Propyl Alcohol | 1.11 | 1.06 | 0.96 | 0.93 | 0.86 | 0.84 | 0.80 |
| Propion-Aldehyde | 0.33 | 0.38 | 0.40 | 0.42 | 0.43 | 0.43 | 0.44 |
| N-Propyl Alcohol | 0.16 | 0.14 | 0.13 | 0.12 | 0.11 | 0.11 | 0.11 |
| Acral-dehyde | 0.13 | 0.14 | 0.14 | 0.15 | 0.15 | 0.15 | 0.15 |
| Allyl Alcohol | 0.044 | 0.044 | 0.041 | 0.038 | 0.038 | 0.037 | 0.036 |

Table 12

Computer Predicted G-Values of the Products Containing Oxygen at Different Oxygen Concentration

| Products | Amount of Added Oxygen | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1% | 3% | 5% | 7% | 10% | 13% | 15% |
| Acetone | 1.13 | 1.09 | 1.05 | 1.02 | 0.98 | 0.96 | 0.94 |
| I-Propyl Alcohol | 1.06 | 1.01 | 0.97 | 0.94 | 0.90 | 0.88 | 0.86 |
| Propion-Aldehyde | 0.31 | 0.35 | 0.37 | 0.40 | 0.43 | 0.46 | 0.47 |
| N-Propyl Alcohol | 0.14 | 0.13 | 0.13 | 0.12 | 0.12 | 0.11 | 0.11 |
| Acral-dehyde | 0.14 | 0.15 | 0.15 | 0.15 | 0.15 | 0.15 | 0.15 |
| Allyl Alcohol | 0.042 | 0.041 | 0.039 | 0.038 | 0.037 | 0.036 | 0.036 |

Table 13

Yield of Primary Processes in the Radiolytic Oxidation of Propane From Computer Modeling Calculation

| Process | G-value |
|---|---|
| (1) $C_3H_8$ -------> $C_3H_8^*$ | 1.00 |
| (2) $C_3H_8$ -------> i-$C_3H_7$• + $H^*$ | 1.55 |
| (3) $C_3H_8$ -------> n-$C_3H_7$• + $H^*$ | 0.47 |
| (4) $C_3H_8$ -------> $C_3H_5$• + H• + $H_2$ | 0.20 |

Table 14

Comparison of Measured and Computed Yields in the Radiolytic Oxidation of Propane

| Product | G-Measured | G-Calculated |
|---|---|---|
| Acetone | 0.98 | 0.98 |
| I-Propyl Alcohol | 0.86 | 0.90 |
| N-Propyl Alcohol | 0.11 | 0.12 |
| Propionaldehyde | 0.43 | 0.43 |
| Acraldehyde | 0.15 | 0.15 |
| Allyl Alcohol | 0.038 | 0.037 |

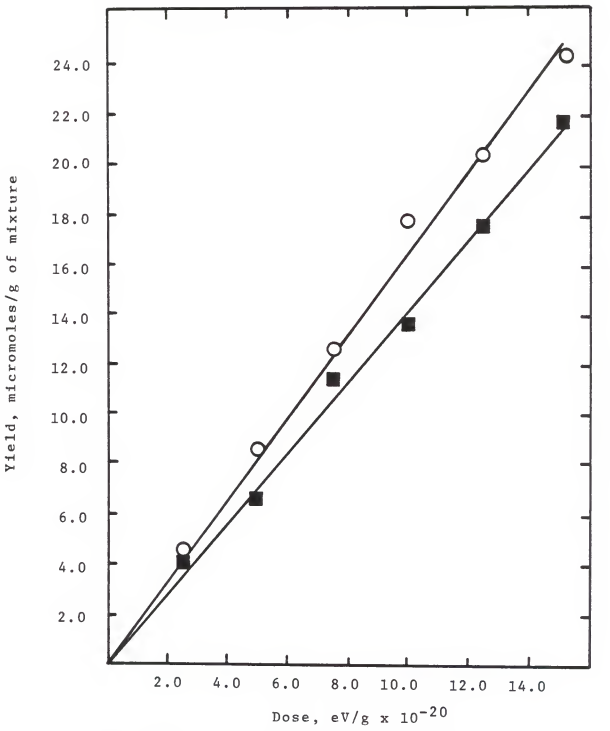



Fig. 23 Production of acetone, ○ and i-propyl alcohol, ■ as a function of dose in the radiolytic oxidation of propane.

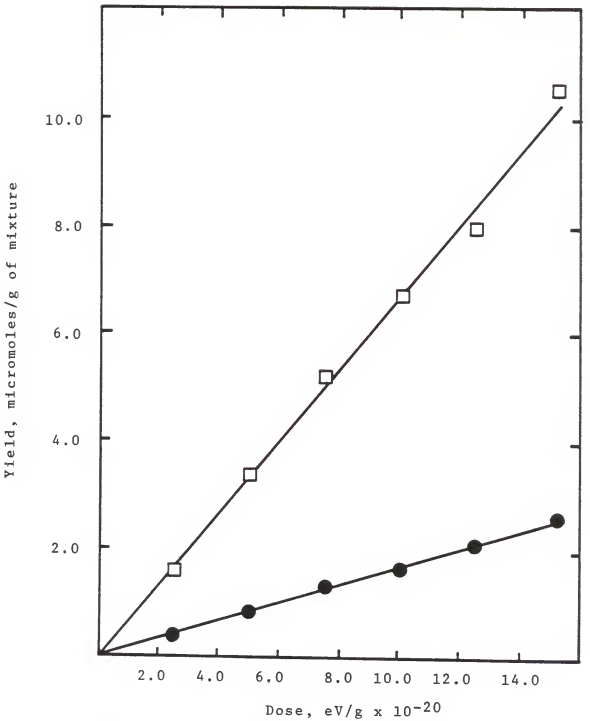



Fig. 24 Production of propionaldehyde □ and n-propyl alcohol ● as a function of dose in the radiolytic oxidation of propane.

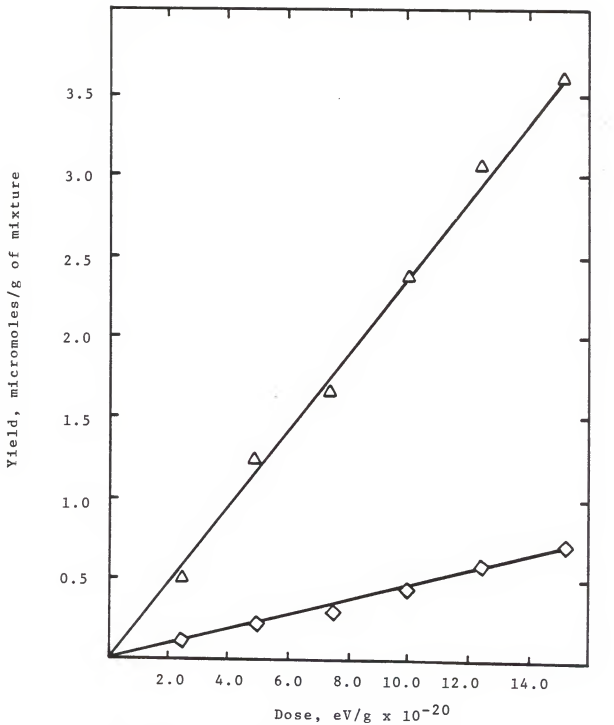



Fig. 25 Production of acraldehyde △ and allyl alcohol ◇ as a function of dose in the radiolytic oxidation of propane.

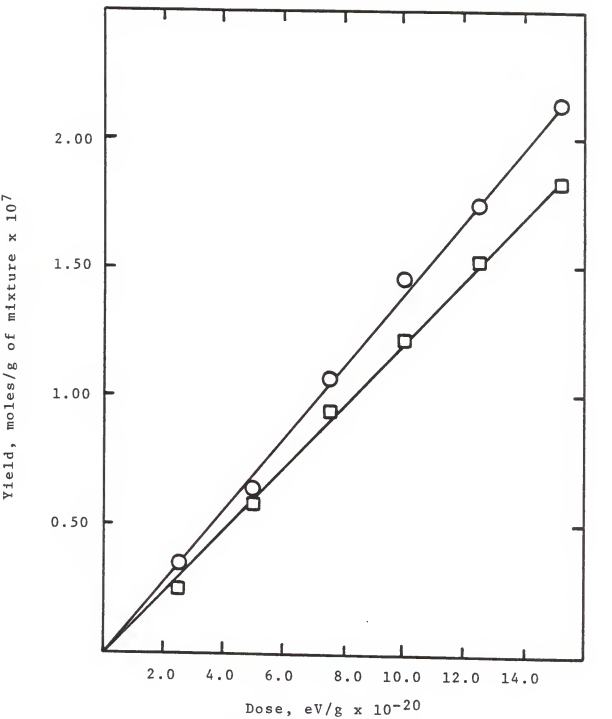



Fig. 26 Production of i-butyl alcohol, ○ and tert-amyl alcohol, □ as a function of dose in the radiolytic oxidation of propane.

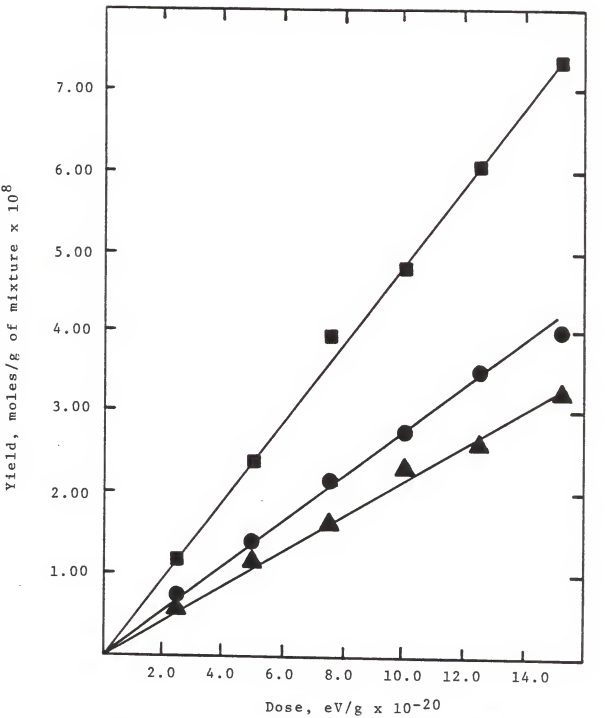



Fig. 27 Production of n-butyl alcohol, ■; n-amyl alcohol, ● and i-amyl alcohol ▲ as a function of dose in the radiolytic oxidation of propane.

alcohol. Small yields of iso-hexyl alcohol and n- hexyl alcohol were also observed. The G-values of various products at 10% added oxygen are listed in Table 9. There was no apparent change in the G-values at pressures of 50, 100, 150 torr. When the concentration of oxygen is varied, it is seen that at lower concentrations of oxygen the yield of acetone, iso-propyl alcohol, and n-propyl alcohol increases, the yield of propionaldehyde decreases while the yield of acraldehyde and allyl alcohol remains the same. This is shown in Figs. 30a and 31a. The G-values of various major oxygen containing products at different concentrations of oxygen at constant dose $10.1 \times 10^{20}$ eV/g are listed in Table 11.

## B. Discussion

If one takes into account all ionic and free radical reaction pathways known to take part in the gamma radiolysis of gas phase propane, the system would appear to be a rather complex one. It might seem that addition of $O_2$ to the system would lead to even greater complexities. In the early stages of interpretation of the data, however, it was discovered that the product spectrum and even relative product yields bear a remarkable resemblance to the species formed in the low temperatures autoxidation of gaseous propane. Accordingly, an attempt was made to interpret the

data on the basis of a simple free radical mechanism. As will be seen below this effort was quite successful in providing both a qualitative and quantitative description of the product spectrum and experimental G-values in the radiolysis of propane oxygen mixtures.

It is reasonable to inquire what is the physical basis for the apparent simplicity of this system; i.e. why is it not necessary to consider ionic reaction pathways in interpreting the results? The most obvious interpretation is to suggest that $O_2$ acts in the system not only to intercept thermal free radicals, but also to capture thermal electrons. In consequence, the high energy neutralization pathways which must be present in the pure system

$$C_3H_8^+ + e^- \text{---> products} \qquad \text{(a)}$$

are replaced with a new neutralization pathway

$$C_3H_8^+ + O_2^- \text{---> products} \qquad \text{(b)}$$

The latter process is characterized by an energy release which is lower to the extent of the electron capture energy of $O_2$. Several consequences would follow; any slow fragmenting processes involving long-lived excited states of $C_3H_8^+$ would be quenched, and fragmentation processess resulting from the relatively high energy neutralization process (a) would be replaced by new reaction pathways subsiquent to the lower energy neutralization process

(b). Not only is the total energy release in process (b) less than process (a), but the exothermicity might be shared by the $C_3H_8^+$ and $O_2^-$ species involved, and in fact the reaction might involve $H^+$ transfer to $O_2^-$, with the consequence that essentially all the energy released involves $O_2^-$ (or neutral $HO_2\cdot$).

It seems clear that addition of $O_2$ serves to quench many ionic processes in the system. This includes not only the prevention of subsequent fragmentation of longer-lived states of $C_3H_8^+$, but also the prevention of subsequent ion-molecule Reaction on the part of first generation fragmentation ions formed from $C_3H_8^+$. While sufficient energy might be released in neutralization step (b) to cause fragmentation of $C_3H_8^*$, the available energy may be sufficiently low to prevent extensive secondary fragmentation. In fact, neutralization via the $H^+$ transfer route appears especially attractive, since this would yield exclusively species with the stoichiometry $C_3H_7\cdot$.

There is another favorable aspect to the model just presented. As described below in connection with computer simulation work, it was observed that the total G-value for all processes modifying $C_3H_8$ is approximately the same in the scavenged and unscavenged system. However, it was found that the detailed primary yields from the unscavenged system could not be carried over without modification to the oxygen scavenged system. An additional aspect of the

situation is that among the processes wiped out by adding oxygen appear to be those processes which in the unscavenged system lead to C-C bond rupture. This observation is perhaps the best evidence that the actual mechanism of neutralization step (b) is the $H^+$ transfer since as noted above this would give only $C_3H_7\cdot$ radical, and would not necessarily give a large deposition of energy in the hydrocarbon. In fact, the neutralization would occur in the $(H^+ \ldots O_2^-)$ reaction complex.

Formation of Products Via Free Radical Mechanism

Oxygen readily adds to alkyl free radicals, to give relatively stable peroxy radicals (36,61).

$$R\cdot + O_2 \longrightarrow R\text{-}O\text{-}O\cdot$$

From the results in Table 9 it is clear that three carbon species predominate among the products; all the species formed with G-values greater than Ø.Ø1 contain three carbon atoms. These species formed can be derived from i-propyl, n-propyl, and allyl radicals.

$$C_3H_8 \longrightarrow C_3H_8^* \quad (1)$$

$$C_3H_8 \longrightarrow i\text{-}C_3H_7\cdot + H^* \quad (2)$$

$$C_3H_8 \longrightarrow n\text{-}C_3H_7\cdot + H^* \quad (3)$$

$$C_3H_8 \longrightarrow C_3H_5\cdot + H_2 + H\cdot \quad (4)$$

The formula $C_3H_8^*$ represents a rather long-lived excited state of $C_3H_8$, which is subject to Reaction with $O_2$ (or collisional quenching by $O_2$); the role of this species is discussed below.

Reactions 2 and 3 are shown as producing hot $H^*$ exclusively, along with n- and i-propyl radicals. It is not critical that some fraction of the hydrogen produced may be thermal, since a portion of the $H^*$ is thermalized in any event. (See Reaction 21 and related discussion given below). Reaction 4 seems to be the most straightforward process leading to the formation of allyl radical, $C_3H_5^\cdot$, which is precursor to two observed products of moderate importance.

These radicals i-$C_3H_7^\cdot$, n-$C_3H_7^\cdot$ and $C_3H_5^\cdot$ formed in Reactions 2, 3, and 4 combine with oxygen to give i-propyl peroxy, n-propyl peroxy and allyl peroxy radicals.

$$i\text{-}C_3H_7^\cdot + O_2 \text{ ---> } i\text{-}C_3H_7\text{-}O\text{-}O^\cdot \quad (5)$$

$$n\text{-}C_3H_7^\cdot + O_2 \text{ ---> } n\text{-}C_3H_7\text{-}O\text{-}O^\cdot \quad (6)$$

$$C_3H_5^\cdot + O_2 \text{ ---> } C_3H_5\text{-}O\text{-}O^\cdot \quad (7)$$

Alkyl peroxy radicals combine pairwise to give alkoxy radicals along with molecular oxygen (36).

$$2\ RO_2^\cdot \text{ ---> } 2\ RO^\cdot + O_2$$

For example, two i-propyl peroxy radicals give iso-propoxy radicals plus molecular oxygen, n-propyl peroxy gives n-propoxy and allyl peroxy gives allyloxy radical products.

$$2\ i\text{-}C_3H_7\text{-}O\text{-}O\cdot \longrightarrow 2\ i\text{-}C_3H_7\text{-}O\cdot + O_2 \qquad (8)$$

$$2\ n\text{-}C_3H_7\text{-}O\text{-}O\cdot \longrightarrow 2\ n\text{-}C_3H_7\text{-}O\cdot + O_2 \qquad (9)$$

$$2\ C_3H_5\text{-}O\text{-}O\cdot \longrightarrow 2\ C_3H_5\text{-}O\cdot + O_2 \qquad (10)$$

The cross-reactions must also occur: $i\text{-}C_3H_7\text{-}O\text{-}O\cdot$ can combine with $n\text{-}C_3H_7\text{-}O\text{-}O\cdot$ or $C_3H_5\text{-}O\text{-}O\cdot$; and $n\text{-}C_3H_7\text{-}O\text{-}O\cdot$ can combine with $C_3H_5\text{-}O\text{-}O\cdot$ to give molecular oxygen and the corresponding alkoxy radicals.

Combination of two alkoxy radicals to give a peroxide appears less probable than disproportionation to give an alcohol and a carbonyl compound (36).

$$2\ RCH_2O\cdot \longrightarrow R\text{-}CH_2\text{-}O\text{-}O\text{-}CH_2\text{-}R \qquad \text{less probable}$$

$$2\ RCH_2O\cdot \longrightarrow RCH_2OH + RCHO \qquad \text{more probable}$$

When two i-propoxy radicals combine the products are acetone and iso-propyl alcohol.

$$2\ i\text{-}C_3H_7O\cdot \longrightarrow \underset{\text{acetone}}{(CH_3)_2C{=}O} + \underset{\text{i-propyl alcohol}}{i\text{-}C_3H_7OH} \qquad (11)$$

Two n-propoxy radicals combine to give propionaldehyde and n-propyl alcohol.

$$2\ n\text{-}C_3H_7O\cdot \longrightarrow \underset{\text{propion-aldehyde}}{CH_3CH_2CHO} + \underset{\text{n-propyl alcohol}}{n\text{-}C_3H_7OH} \qquad (12)$$

When an i-propoxy radical combines with a n-propoxy radical the products are either (a) acetone and n-propyl alcohol, or (b) propionaldehyde and iso-propyl alcohol.

$$i\text{-}C_3H_7O\cdot + n\text{-}C_3H_7O\cdot \longrightarrow \underset{\text{acetone}}{(CH_3)_2C{=}O} + \underset{\text{n-propyl alcohol}}{n\text{-}C_3H_7OH} \qquad (13)$$

$$i\text{-}C_3H_7O\cdot + n\text{-}C_3H_7O\cdot \longrightarrow \underset{\text{iso-propyl alcohol}}{i\text{-}C_3H_7OH} + \underset{\text{Propion-aldehyde}}{CH_3CH_2CHO} \qquad (14)$$

An i-propoxy radical can combine with an allyloxy radical in two ways to give
a) acetone and allyl alcohol or b) i-propyl alcohol and acraldehyde.

$$i\text{-}C_3H_7O\cdot + C_3H_5O\cdot \longrightarrow \underset{\text{acetone}}{(CH_3)_2C{=}O} + \underset{\text{allyl alcohol}}{CH_2{=}CHCH_2OH} \qquad (15)$$

$$i\text{-}C_3H_7O\cdot + C_3H_5O\cdot \longrightarrow \underset{\text{i-propyl alcohol}}{I\text{-}C_3H_7OH} + \underset{\text{acraldehyde}}{CH_2{=}CHCHO} \qquad (16)$$

A n-propoxy radical can react with an allyloxy radical in two ways to give

a) propionaldehyde and allyl alcohol b) i-propyl alcohol and acraldehyde.

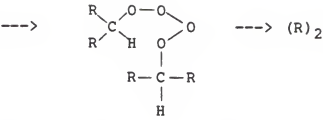
$$n\text{-}C_3H_7O^{\cdot} + C_3H_5O^{\cdot} \longrightarrow \underset{\text{Propion-aldehyde}}{CH_3CH_2CHO} + \underset{\text{allyl alcohol}}{CH_2{=}CHCH_2OH} \qquad (17)$$

$$n\text{-}C_3H_7O^{\cdot} + C_3H_5O^{\cdot} \longrightarrow \underset{\text{i-propyl alcohol}}{i\text{-}C_3H_7OH} + \underset{\text{acraldehyde}}{CH_2{=}CHCHO} \qquad (18)$$

Two allyloxy radical can react to give acraldehyde and allyl alcohol.

$$2\ C_3H_5O^{\cdot} \longrightarrow \underset{\text{acraldehyde}}{CH_2{=}CH_2CHO} + \underset{\text{allyl alcohol}}{CH_2{=}CHCH_2OH} \qquad (19)$$

Allyl alcohol and acraldehyde are formed by Reactions 15, 16, 17, 18 and 19. The above Reactions 11 through 19 explain the formation of the major products like acetone, i-propyl alcohol, propionaldehyde, n-propyl alcohol, acraldehyde, and allyl alcohol. In the reaction sequence just presented, conversion of two peroxy radicals to alkoxy radicals, and subsequent conversion of two alkoxy radicals to an alcohol and a carbonyl compound was shown as two separate steps. A mechanism is known, however, which combines these two processes. In the "Russel mechanism", two peroxy radicals can combine to give a cyclic transition state, which subsequently fragments to give a carbonyl compound, an alcohol, and molecular oxgen (77).



Although this process is interesting from the mechanistic viewpoint, it does not lead to any new or different predictions regarding product formation.

Hot hydrogen atoms born in Reactions 2 and 3 may react while hot, or may become thermalized.

$$H^* + O_2 \longrightarrow HO_2^\bullet \qquad (20)$$

$$H^* + C_3H_8 \longrightarrow i\text{-}C_3H_7^\bullet + H_2 \qquad (21)$$

$$H^* + C_3H_8 \longrightarrow n\text{-}C_3H_7^\bullet + H_2 \qquad (22)$$

$$H^* + C_3H_8 \longrightarrow C_3H_8 + H^\bullet \qquad (23)$$

In most cases the fate of thermal hydrogen atoms is reaction either with substrate or oxygen. At this point, however, the difference in energy between primary and secondary C-H bonds becomes significant; abstraction by thermal hydrogen atoms gives predominantly $i\text{-}C_3H_7^\bullet$.

$$H^\bullet + C_3H_8 \longrightarrow i\text{-}C_3H_7^\bullet + H_2 \qquad (24)$$

$$H^\bullet + O_2 \longrightarrow HO_2^\bullet \qquad (25)$$

Perhydroxyl radicals formed in Reactions 20 and 25 combine to give hydrogen peroxide, the yield of which was not measured.

$$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \qquad (26)$$

Since the yields of the carbonyl compounds are greater than the corrosponding alcohols, the carbonyl compounds are formed in some other way besides Reactions 11, 12, 13, 14, 15, 16, and 19. A perhydroxyl radical can also abstract a hydrogen atom from i-propoxy, n-propoxy or allyloxy radicals to give acetone, propionaldehyde and acraldehyde.

$$i\text{-}C_3H_7O^{\bullet} + HO_2^{\bullet} \longrightarrow \underset{\text{acetone}}{(CH_3)_2C{=}O} + H_2O_2 \qquad (27)$$

$$n\text{-}C_3H_7O^{\bullet} + HO_2^{\bullet} \longrightarrow \underset{\substack{\text{Propion-}\\\text{aldehyde}}}{CH_3CH_2CHO} + H_2O_2 \qquad (28)$$

$$C_3H_5\emptyset^{\bullet} + HO_2^{\bullet} \longrightarrow \underset{\text{Acraldehyde}}{CH_2{=}CHCHO} + H_2O_2 \qquad (29)$$

Reactions 27, 28, and 29 explain why the yield of acetone is greater than iso-propyl alcohol, propionaldehyde is greater than n-propyl alcohol and acraldehyde greater than allyl alcohol.

All the reactions above account for the formation of major products at high concentrations of oxygen. At low concentrations of oxygen it is seen from Figs. 30a and 31a that the yields of acetone, iso-propyl alcohol and n-propyl alcohol increase, the yield of propionaldehyde decreases,

while the yield of acraldehyde and allyl alcohol remains the same. This can be explained as follows:

At low concentrations of oxygen the hot hydrogen atoms are less efficiently scavenged by oxygen. Instead, the hot hydrogen abstracts a hydrogen atom from the substrate to give $i\text{-}C_3H_7^{\bullet}$ and $H_2$, as explained earlier. The consequent excess production of $i\text{-}C_3H_7^{\bullet}$ (and subsequently $i\text{-}C_3H_7O_2^{\bullet}$ and $i\text{-}C_3H_7O^{\bullet}$) as compared to $n\text{-}C_3H_7^{\bullet}$ (plus $n\text{-}C_3H_7O_2^{\bullet}$ and $n\text{-}C_3H_7O^{\bullet}$) accounts for enhanced yield of acetone and i-propyl alcohol as oxygen concentration falls off. The n-propyl alcohol yield increases slightly at low oxygen concentrations due to the cross-reaction with i-propoxy radicals.

It might appear that the propionaldehyde yield should also increase at low oxygen concentrations, due to cross-reaction 13 and 14. From experimental results, however, it was known that this yield decreases at low oxygen concentration. A large number of computer simulation runs was made in an attempt to clarify this point. It was found that no reasonable combination of rate constants for reactions considered up to this point could explain the experimental fact (fall-off of propionaldehyde at low oxygen concentration), although some combinations of parameters gave a propionaldehyde yield which was nearly independent of oxygen concentration.

A review of the published literature on radiolytic oxidation of hydrocarbons provided a possible resolution of the propionaldehyde yield problem. In interpreting the results of liquid-phase radiolytic oxidation of n-heptane, Kunjappu and Rao (60) suggested a direct reaction between molecular oxygen and excited n-heptane to give heptanones.

$$C_7H_{16}^* + O_2 \longrightarrow C_7H_{14}O + H_2O$$

A similar postulate is capable of explaining the present results; a reaction of $C_3H_8^*$ with $O_2$ to give propionaldehyde and water is suggested.

$$C_3H_8^* + O_2 \longrightarrow CH_3CH_2CHO + H_2O \qquad (30)$$

The yield of this reaction would be expected to fall-off at low oxygen concentration, since Reaction 30 must compete with other oxygen independent channels for loss of $C_3H_8^*$.

Since the concentration of allyl radicals does not change at various concentrations of oxygen, there is not much change in the yields of allyl alcohol and acraldehyde as a function of oxygen concentration. The yields of the latter products are relatively small compared to acetone, propionaldehyde, iso-propyl alcohol, and n-propyl alcohol in any event.

Computer Simulation of Radiolytic Oxidation Mechanism

Since the entire reaction mechanism too complex to be suitable for modeling, several simplifications were made in selecting the subset of 28 reactions given in Table 10 as the basis for the computer work. This scheme involves G-values for only 4 postulated primary processes, along with 24 rate constants for subsequent thermal and hot radical reactions. Unfortunately, only 8 of needed rate constants were available from the literature (68,69,71,74-76), and several of these had a broad range of uncertainty.

The numbers of "degrees of freedom " in dealing with the mechanisn is considerably less than the total number of unknown rate constants involved. This is true mainly because each species has only two or three reaction channels by which it is consumed; only the ratio of the respective rate constants affects the predictions made by computer modeling. There is also some limitation on the rate constants selected, in that the numbers must be of approximate magnitude for radical-radical reactions, radical-oxygen reactions, hydrogen abstraction from substrate, etc.

Several of the simplifications made in choosing the reaction scheme for computer modeling were discussed above, particularly the elimination of ionic processes for further consideration. Some additional simplifications were made

for entirely pragmatic reasons. For example, cross-combination reactions between the three peroxy radicals (i-$C_3H_7O_2^{\bullet}$, n-$C_3H_7O_2^{\bullet}$, and $C_3H_5O_2^{\bullet}$) to form the corresponding alkoxy radicals and molecular oxygen were ignored, since including the necessary three reactions would add little new information. Additionally, where reactions of hydroperoxy radicals ($HO_2^{\bullet}$) with the three alkoxy radicals shown, reactions of $HO_2^{\bullet}$ with the alkyl peroxy species was excluded arbitrarily. Also, the disproportionation reaction of 2 n-$C_3H_5O^{\bullet}$ radicals to give the corresponding aldehyde and alcohol is shown, but the cross-reactions with i-$C_3H_7O^{\bullet}$ and n-$C_3H_7O^{\bullet}$ are ignored, as a matter of convenience. Even with these simplifications, the entire scheme is rather complex.

More then 100 computer runs were made using various combinations of mechanistic reactions and their rate constants. The best results were obtained by using the combination of mechanistic steps and rate constants given in Table 9. Tables 11 and 12 show the experimental and computer predicted G-values of the radiolysis products at different oxygen concentrations. Table 12 shows G-values of major primary processes, as inferred from computer modeling work. Table 13 gives a comparison of the measured and calculated G-values for major products, as derived from Tables 11 and 12 for the case of 10% oxygen. Figures 28 and

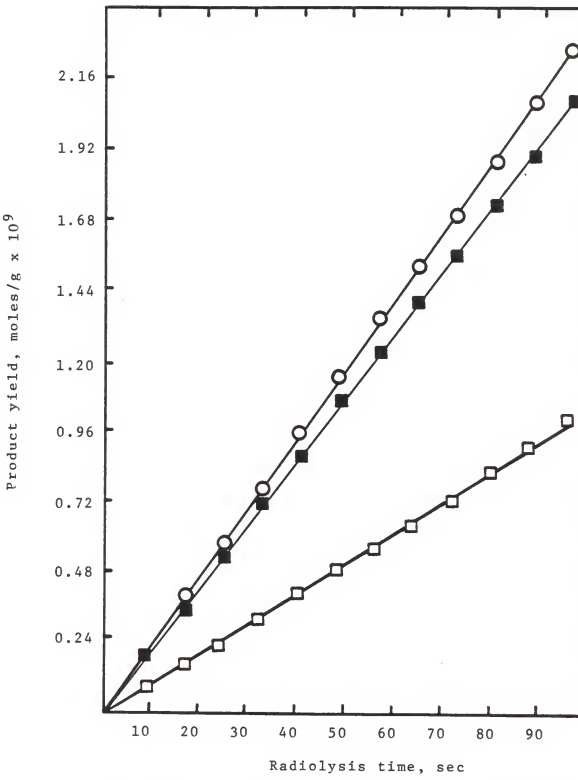



Fig. 28 Computer predicted yields of acetone, ○ ; i-propyl alcohol, ■ and propionaldehyde, □ as a function of radiolysis time.

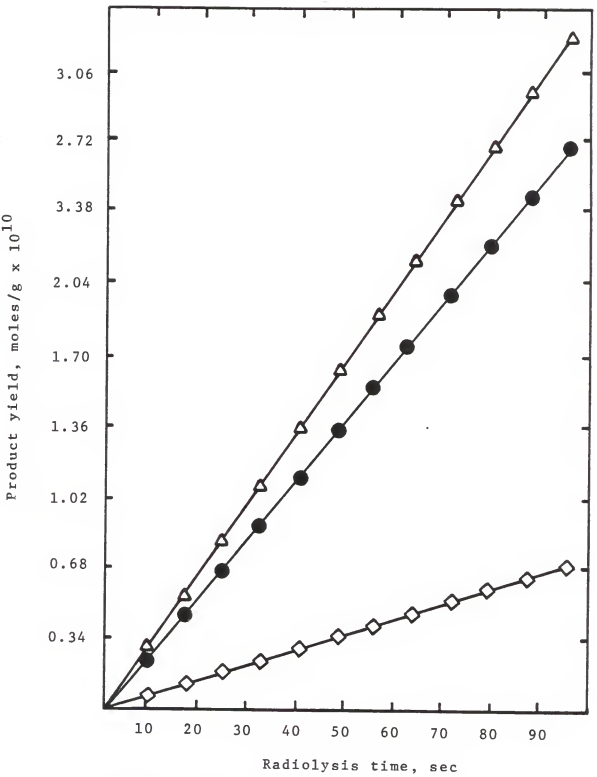



Fig. 29 Computer predicted yields of acraldehyde, △ ; n-propyl alcohol, ● and allyl alcohol ◇ as a function of radiolysis time.

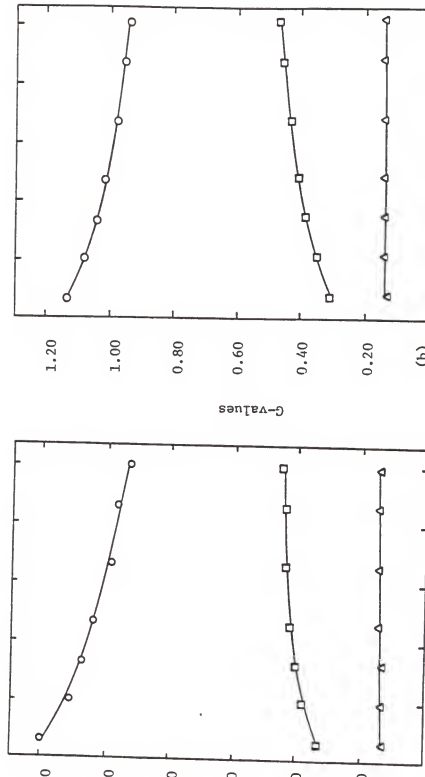



Fig. 30 Experimental and Computer predicted G-values of acetone, ○; propionaldehyde, □ and acraldehyde, △ as a function of added oxygen in the radiolytic oxidation of propane. (a) Experimental G-values (b) Computer predicted G-values

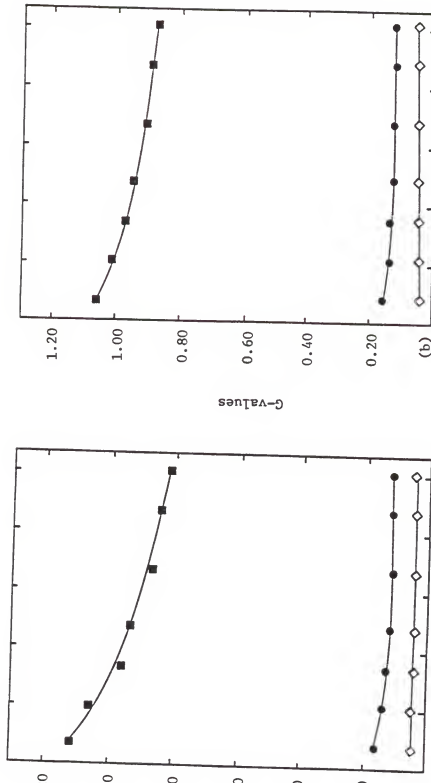



Fig. 31 Experimental and Computer predicted G-values of i-propyl alcohol, ■ ; n-propyl alcohol, ● and allyl alcohol, ◇ ; as a function of added oxygen in the radiolytic oxidation of propane. (a) Experimental G-values (b) Computer predicted G-values

29 show the computer predicted yields of major oxygen containing products as a function of radiolysis time, over a time period of 100 seconds. The computations could be extended to a longer time, by using more iterations, but it was not feasible to increase the time increment per computer step, since behavior of the concentration of transient species become erratic if the $\Delta T$ per computer increment represents an excessively long time compared with the half lives of the radical processes. Figures 30a, 30b, 31a, and 32b compare experimentally measured and computed yields of the oxygenated products as a function of percent of added oxygen in the radiolytic oxidation of propane. It will be seen that the computer modeling scheme provides a very satisfactory interpretation of the experimental data.

A typical printout made during one run of the numerical integration program is given in Appendix V; it shows the steady state and net product, mechanistic steps, their rate constants, and the concentrations of several products at various time periods. Each print interval represents 10 increments of the integrated package, so that the printout showing 50 print intervals represents 500 iterations of the program.

## C. Summary

The radiolytic oxidation of gaseous propane was studied at 100 torr pressure at various concentrations of

oxygen at 25 °C. The major oxygen containing products and their G-values when 10% oxygen was added to propane were acetone, 0.98 ; i-propyl alcohol, 0.86; propionaldehyde, 0.43; n-propyl alcohol, 0.11; acraldehyde, 0.14; and allyl alcohol 0.038. The minor products were iso-butyl alcohol, tert-amyl alcohol, n-butyl alcohol, n-amyl alcohol, and iso-amyl alcohol. Small yields of iso-hexyl alcohol and n-hexyl alcohol were also observed. There was no apperent change in the G-values at pressures of 50, 100, and 150 torr. The formation of major products was explained on the basis that the radicals H·, i-$C_3H_7$·, n-$C_3H_7$·, and $C_3H_5$·, combine with $O_2$ to give peroxy radicals $HO_2$·, i-$C_3H_7O_2$·, n-$C_3H_7O_2$·, and $C_3H5O_2$·. The peroxy radicals i-$C_3H_7O_2$, n-$C_3H_7O_2$·, and $C_3H5O_2$· react with one another to give the corresponding alkoxy radicals i-$C_3H_7O$·, n-$C_3H_7O$· and $C_3H5O$·.

These alkoxy radicals react with one another to give carbonyl compounds and alcohol. Hydroperoxy radical also reacts with the alkoxy radicals to give the corresponding carbonyl compounds. It is suggested that propionaldehyde, which is one of the major products, is also formed directly by reaction of excited propane and oxygen. The reaction scheme for the formation of major products, at various concentrations of oxygen, was examined by computer modeling based on a mechanism involving 28 reactions. Yields could

be brought into agreement with the data within experimental error in nearly all the cases.

One conclusion which emerged quite clearly from comparative work on pure propane and propane-oxygen systems is the following: it is not possible to choose a single set of "primary yields" which is appropriate for pure propane and for propane heavily scavenged with oxygen (1-15% concentration). It appears obvious that addition of oxygen at these concentration levels interferes with species which act as precursors to the radical (and to a lesser extent molecular) yields, in the unscavenged system. Nevertheless, it is of interest that the total G-values for the primary processes are quite similar in pure propane and propane-oxygen system, 7.6 and 8.5 respectively.

Only a single type of propyl radical was assumed for the pure propane system. It was necessary to distinguish between normal propyl and iso-propyl radicals in the case of propane-oxygen mixtures, since the behavior of the two species is distinctly different when oxygen is added to the system. Normal propyl radical is precursor to propionaldehyde and n-propyl alcohol, while iso-propyl radical is a precursor to iso-propyl alcohol and acetone.

Another feature of this work concerns the apparent absence of oxygenated species containing less than three carbon atoms. Similarly Kunjappu and Rao in the radiolytic oxidation of n-heptane found essentially a total lack of

oxygenated products containing fewer carbon atoms than the parents.

# APPENDIX I

## CALCULATION OF DOSIMETRY

Unlike a typical liquid phase radiolysis where the incident gamma rays interact directly with the liquid, the usual case in a gas phase radiolysis is to find that the incident gamma rays interact mainly with the walls of the vessel and the ejected electrons in turn irradiate the gas. If the vessel meets certain geometric criterion, which are below, it can be considered to be a Brag-Gray cavity (78,79). This means that the ionization in the cavity is produced by secondary electrons and that energy deposition in gases in the cavity depends on their electron stopping power, rather than their electron densities.

The nickel radiolysis vessels used in the work can be shown to meet the requirements for a Bragg-Gray cavity as outlined by Hine and Brownell (66).

1. The cavity must have dimensions such that only a very small fraction of the particle energy is dissipated in it. This also means that only a very small fraction of the particles contributing to the ionization will enter the cavity with a range smaller than the cavity dimensions.

The radiolysis vessel (Fig. 5) has an internal diameter of 3.8 cm. In a typical experiment, the ethylene pressure was 300 torr, which was used as a dosimeter. This corresponds to a density of $4.52 \times 10^{-4}$ g/cc. The average energy of compton electrons produced by Co-60 gamma rays is 0.587 MeV. These electrons have a range of 0.207 g/cm$^2$ in ethylene (80). Dividing this value by the density of ethylene gives a range of 4.58 meters. Thus the average secondary electron easily traverses the radiolysis cell.

2. Direct absorption of quantum radiation by the gas in the cavity should contribute only a negligible portion of the total ionization (66).

The gamma rays from Co-60 have energies 1.17 MeV and 1.32 MeV. In this region of energies the cross section for the photoelectric effect and for pair production are very small compared to the cross section for compton scattering. Thus the relative energy absorption of the nickel walls and the gas inside is proportional to the ratio of their electron densities. The electron densities of nickel and ethylene at 300 torr are $2.56 \times 10^{24}$ electron/cc and $1.56 \times 10^{20}$ electron/cc respectively. The ratio of these values is about $10^4$. This indicates negligible absorption by the gas compared to the walls of the vessel.

3. The cavity must be surrounded by an equilibrium thickness of solid medium so that all the particles crossing it originate in the medium. The required thickness for electronic equilibrium is theoretically equal to the range of the

particle of maximum energy released in the medium, although in practice path obliquity leads to the approximate establishment of electronic equilibrium at a wall thickness of considerably less than the maximum range (66).

The range of a 1.3 MeV electron in nickel is about 0.5 mm. Thus the 1.19 mm thick walls of the vessel are sufficient to establish electronic equilbrium.

4. The energy dissipated by the ionizing particles must be sensibly uniform over the volume of the medium immediately surrounding the cavity and contributing to the electronic equilibrium (66).

This criterion should not be critical in the determination of comparative rather than absolute dose rates, and all that was necessary in the present work was to know the total dose rate averaged over the volume of the vessel.

Now it is possible to relate the energy deposited in the gas used as a dosimeter ($E_D$) to that deposited in some other gas of interest ($E_S$) by multiplying by the ratio of their electron stopping powers.

$$E_S = \frac{S_S}{S_D} \times E_D$$

where $S_S$ and $S_D$ are the mass stopping powers of the gas sample and dosimeter respectively. The mass stopping power is defined as

$$S = - \frac{dE}{dx} \times \frac{1}{\rho} \quad \text{erg cm}^2/\text{g}$$

where $\rho$ is the density of the medium and $-(dE/dx)$, usually known as the specific energy loss or stopping power, is the energy loss per unit path length by a particle crossing the medium. This value can be calculated by using the Bethe equation, which has the form (36)

$$\frac{dE}{dx} = \frac{2\pi Ne^4 Z}{m_o v} \left\{ \ln \frac{m_o v^2 E}{2I^2(1-\beta^2)} - [2(1-\beta^2)^{1/2} - 1 + \beta^2] \ln 2 \right.$$

$$\left. + 1 - \beta^2 + \frac{1}{8} [1-(1-\beta^2)^{1/2}]^2 \right\} \text{ erg/cm}$$

When applied to molecules, the symbols have the following meanings:

$N$ = number of molecules/cm$^3$

$m_o$ = rest mass of electron

$\beta$ = v/c = ratio of electron velocity to that of light

$e$ = charge on electron

$Z$ = atomic number or number of electrons per molecule

$v$ = velocity of electron

$I$ = mean excitation potential

Taking the ratio of the stopping power of the sample ($S_S$) to that of the dosimeter ($S_D$) and rearranging the terms in the brackets gives

$$\frac{S_S}{S_D} = \frac{(N_S Z_S)(k - \ln I_S^2)}{(N_D Z_D)(k - \ln I_D^2)}$$

$$\frac{E_S}{E_D} = \frac{S_S}{S_D} = \frac{(P_S Z_S)(k - \ln I_S^2)}{(P_D Z_D)(k - \ln I_D^2)}$$

where $$k = \ln \frac{m_o v^2 E}{2(1-\beta^2)} - [2(1-\beta^2)^{1/2} - 1 + \beta^2)]\ln 2 + 1$$

$$- \beta^2 + \frac{1}{8}[1-(1-\beta^2)^{1/2}]^2$$

$P_S$ and $P_D$ are the pressures of the gas sample and doeimeter respectively.

The average energy of a Co-60 gamma ray source is 1.25 MeV (average of 1.17 and 1.33 MeV). The average energy of the Compton electrons generated by scattering of a 1.25 MeV gamma ray is

$$E_{av} = \frac{\sigma_a}{\sigma} \times E_{(photon)}$$

where $\sigma$ is the total Compton cross section per electron

$\sigma_a$ is the cross section for energy absorbed per electron

$\sigma = 1.892 \times 10^{-25}$ cm$^2$/electron

$\sigma_a = 0.899 \times 10^{-25}$ cm$^2$/electron

$$E_{av} = \frac{(0.899 \times 10^{-25})}{(1.892 \times 10^{25})} \times 1.25 \text{ MeV}$$

$= 0.587$ MeV

$= 9.404 \times 10^{-7}$ erg

From the relativistic energy relation

$$E = mc^2 = \frac{[m_o c^2]}{(1-\beta^2)^{1/2}} - m_o c^2$$

$$\beta = [1 - (\frac{m_o c^2}{E+m_o c^2})^2]^{1/2}$$

Substituting the values

$m_o = 9.1095 \times 10^{-25}$ g

$c = 2.9979 \times 10^{10}$ cm/sec

$E = 9.404 \times 10^{-7}$ erg

We get

$\beta = 8.851 \times 10^{-1}$

$v = c = 2.653 \times 10^{10}$ cm/sec

Using the above constants, k may be evaluated

$$\ln \frac{[m_o v^2 E]}{2(1-\beta^2)} = -27.300 \quad \text{(a)}$$

$$-\ln 2[2(1-\beta^2)^{1/2} - 1 + \beta^2] = -0.4950 \quad \text{(b)}$$

$$1-\beta^2 = 0.2166 \quad \text{(c)}$$

$$\frac{1}{8}[1-(1-\beta^2)^{1/2}]^2 = 0.0357 \quad \text{(d)}$$

$$k = a + b + c + d = -27.5427$$

Values for the mean excitation potentials ($\bar{I}$) for ethylene and propane were calculated from values for the atoms (79), using the relation

$$\ln\bar{I} = \frac{(\Sigma N_i Z_i \ln I_i)}{(\Sigma N_i Z_i)}$$

where

$N_i$ = number of atoms of "i" per molecule

$Z_i$ = atomic number of element "i"

$I_i$ = average excitation potential of element "i"

Values for $I_i$ can be obtained from Hine and Brownell (79) and J. E. Tumer, Patricia D. Roecklein and R. B. Vora (81).

| Element | Z | I(eV) | I(erg) |
|---|---|---|---|
| Hydrogen | 1 | 18.2 | $2.91564 \times 10^{-11}$ |
| Carbon | 6 | 81.3 | $1.30243 \times 10^{-10}$ |
| Oxygen | 8 | 101 | $1.61802 \times 10^{-10}$ |

Average values ($\bar{I}$) for ethylene, propane and oxygen were 55.92 eV, 51.30 eV and 101 eV, using these values of I, the stopping power ratio was found by using equation

$$\frac{E(C_3H_8)}{E(C_2H_4)} = \frac{S(C_3H_8)}{S(C_2H_4)} = 1.62 \times \frac{P(C_3H_8)}{P(C_2H_4)}$$

$$\frac{E(O_2)}{E(C_2H_4)} = \frac{S(O_2)}{S(C_2H_4)} = 1.03 \times \frac{P(O_2)}{P(C_2H_4)}$$

where P is the pressure of the gas.

The total dose in a mixture of gases can be obtained by summing the doses of the individual component

$$E_T = E(C_3H_8) + E(O_2) = \frac{E(C_2H_4)}{P(C_2H_4)} \times [1.62P(C_3H_8) + 1.03P(O_2)]$$

To find the G-value i.e. number of molecules formed per 100 eV energy absorbed

$$G = \frac{\text{molecules}}{\text{eV}} \times 100$$

$$G = \frac{(\text{molecules/gh}) \times 100}{(\text{eV/gh})}$$

$$\frac{\text{molecules}}{\text{gh}} = \frac{G}{100} \times \frac{\text{eV}}{\text{gh}}$$

$$\frac{\text{moles}}{\text{gh}} = \frac{G}{100} \times \frac{\text{eV}}{\text{gh}} \times \frac{1}{N_o}$$

$$G = \frac{(\text{moles/gh}) \times 100 \times N_o}{(\text{eV/gh})}$$

where $N_o$ = Avogadro's number and G for hydrogen in ethylene dosimetry is taken as 1.2 (64,65).

## APPENDIX II

### INTERACTION OF GAMMA RAYS WITH MATTER

Gamma rays are electromagnetic radiations similar to x-rays, but typically of shorter wavelength. A significant difference between x-rays and gamma rays is the source. The source for x-rays is extranuclear, that of gamma rays intranuclear. X-rays result from transitions between electronic energy levels, gamma rays on the other hand are associated with transitions between nuclear energy levels. Gamma rays like x-rays are highly penetrating, the effective range depends on the energy.

The absorption of gamma rays in matter occurs by mechanisms which are completely different from the absorption of charged particles. The interaction is mainly with the atomic electrons, but a gamma ray can lose a large fraction of its energy or all of it in a single encounter. The rays are absorbed according to an exponential law which is characterized by a half thickness ($X_{1/2}$) and absorption coefficient ($\mu$). If $I_o$ is the initial intensity of a beam of gamma rays, then the intensity (I) of rays of initial energy after passing through X cm of absorber will be

$$I = I_o e^{-\mu X}$$

The linear absorption coefficient ($\mu$) is a function of the energy of the gamma rays and the absorbing medium. Half thickness ($X_{1/2}$) is related to linear absorption coefficient by the equation

$$X_{1/2} = \frac{\emptyset.693}{\mu}$$

Gamma rays interact with matter in several ways, photoelectric effect, Compton effect and pair production are of major importance while Rayleigh scattering, photo-disintegration or nuclear reactions and nuclear resonance scattering are of less importance.

1. Photoelectric Effect : It is the most significant for gamma rays of low energy and for absorbers of high atomic number. The inelastic collision of the photon with orbital electron results in the complete ejection of the electron and production of an ion pair. The absorbed photon vanishes. If E is the energy is the gamma ray photon, then in a photoelectric encounter an amount P, equal to the binding energy of the electron in the atom, will be required to remove the electron and the remainder (E-P) is carried off by the electron in the form of kinetic energy

$$K.E. = E-P$$

$$(1/2)mv^2 = h\nu-P$$

In this process the electron most probably comes from the K shell, provided the gamma-ray has sufficient energy to supply the K shell binding energy. The photoelectric absorption follows the equation

$$\text{Probability of photoelectric absorption} \propto Z^5/(E_\gamma^{7/2})$$

Hence it is most important for absorption of low energy gamma in heavy elements.

2. Compton Effect: This is important for gamma rays of medium energy (Ø.5 to 1 MeV) and when the absorber is a material of low atomic number. It involves a collision between a photon and an electron in which a part of the energy of the photon is imparted to the electron. The photon emerges from the collision in a new direction and with reduced energy. The photon of lower energy may then undergo a further photoelectric or Compton interaction, or the energy may be so greatly diminished that it is longer detectable.

The Compton effect is shown in Fig. 32. Considering that both energy and momentum must be conserved in the collision

$$E_I = E_c + E_e \quad (1)$$

$$E_I/c = (E_c\cos\theta)/c + P\cos\phi \quad (2)$$

$$(E_c\sin\theta)/c = p\sin\phi \quad (3)$$

The first equation follows from the conservation of energy. The second equation represents the conservation of momentum along the direction of the incident photon; the momentum of the electron is p, and the momentum of a photon of energy E is E/c. The third equation expresses the conservation of momentum at $90^{o}$ to the direction of the incident photon. The momentum of the electron is related is its kinetic energy $E_e$ by the relativistic in equation

$$p^2 = (1/c^2)\ [E_e(E_e + 2mc^2)]$$

where m is the mass of an electron at rest.

The above equation, with equations 1,2 and 3 may be used to eliminate p, $E_e$ and Q, with the result

$$\lambda_C - \lambda_I = (h/mc)(1 - \cos\phi)$$

where $\lambda_I$ and $\lambda_C$ are wavelengths of the incident and Compton scattered photons. The term h/mc is called compton wavelength and has a value $2.43x10^{-10}$ cm.

The mass absorption coefficient due to Compton scattering varies very little with the atomic number of the absorber. Compton scattering makes only a small contribution to the absorption of high energy photons.

3. Pair Production: Photons of energy greater than 1.Ø2 MeV may be absorbed by pair production. The photon vanishes to be replaced by an electron positron pair whose kinetic energies $E_e$ and $E_p$ are related to the incident photon energy $E_I$ by the equation

$$E_I = E_e + E_p + 2mc^2$$

The $2mc^2$ (1.Ø2 MeV) represents the mass energy which must be supplied to create the particles. The process is not exactly the reverse of electron-positron annihilation, because in that process two photons are emitted, where as in pair production, only one is absorbed. The positron is slowed down in a similar manner to an electron, and eventually combines with an electron, the two particles being replaced by two Ø.51 MeV gamma rays (annihilation radiation) emitted in opposite directions.

In order to simultaneously conserve momentum and energy in pair production, a third body (usually a nucleus) must be present. In the annihilation process, energy and momentum are conserved simultaneously by the emission of two photons. The importance of pair production increases slowly for photon energies above 1.Ø2 MeV. The probability of pair formation increases with the square of the atomic number of the absorbing material. In heavy elements and high energy photons, pair production is much more important than the photoelectric and Compton effects.

4. Rayleigh Scattering: If the interaction between a photon and an orbital electron is insufficient to produce ionization or excitation, the collision is elastic and the energy of the photon is the same after the collision as it was before. Rayleigh scattering rarely results in scattering of the photon through more than a few degrees.

5. Photodisintegration or Photonuclear Reactions: Here the interaction involves a collision of a high energy photon (above 8 MeV) with a nucleus. The photon is completely absorbed in the process, and a neutron, photon or alpha particle is ejected the excited nucleus.

6. Nuclear Resonance Scattering: If the vibrational frequency of a nucleus is equal to that of an incident photon, obsorption of the photon may occur. The photon is then re-emitted from the nucleus. All these interactions are summarized in Table 15.

Table 15

Interaction of Radiation with Matter

| Incident Radiation | In Collision with | Type of Collision | | |
|---|---|---|---|---|
| | | Elastic | Inelastic | Complete Absorption |
| Gamma | Nucleus | | Nuclear Resonance | Photo-disintegration |
| | Orbital Electron | Raleigh Scattering | Compton Effect | Photoelectric Effect |
| | Field | | | Pair Production |

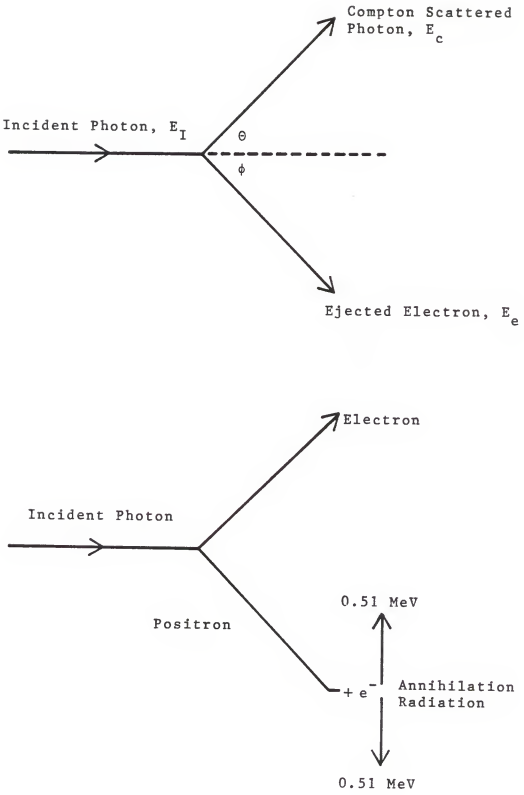



Fig. 32 The Compton effect and Pair-production

## APPENDIX III

### RELATIVE FLAME IONIZATION DETECTOR RESPONSE OF PRODUCTS IN THE RADIOLYSIS OF PROPANE AND IN THE RADIOLYTIC OXIDATION OF PROPANE

In the radiolysis of propane, prior to each analysis, the response of the flame ionization detector was determined using gaseous propane as standard. Flame ionization detector is not sensitive to hydrogen; it was measured using thermal conductivity detector.

In the radiolytic oxidation of propane, acetone was used as a standard. The relative flame ionization detector response on Tracor 550 gas chromatograph are given in Tables 16 and 17.

Table 16

Flame Ionization Detector Response of Products Relative to Propane on Tracor 550 Gas Chromatograph

| | |
|---|---|
| Methane | 0.372 |
| Ethane | 0.737 |
| Propane | 1.00 |
| I-Butane | 1.24 |
| N-Butane | 1.24 |
| I-Pentane | 1.71 |
| N-Pentane | 1.71 |
| Hexane | 2.13 |
| Heptane | 2.24 |
| Octane | 2.41 |
| Nonane | 2.52 |
| Decane | 2.67 |

Table 17

Flame Ionization Detector Response of Products Relative to Acetone on Tracor 550 Gas Chromatograph

| | |
|---|---|
| Propionaldehyde | 0.73 |
| Acetone | 1.00 |
| Iso-Propyl Alcohol | 1.39 |
| N-Propyl Alcohol | 1.39 |
| Acraldehyde | 1.13 |
| Allyl Alcohol | 1.38 |
| Iso-Butyl Alcohol | 2.41 |
| N-Butyl Alcohol | 2.75 |
| Tert-Amyl Alcohol | 2.69 |
| Iso-Amyl Alcohol | 3.69 |
| N-Amyl Alcohol | 3.60 |

## APPENDIX IV

### DETAR KINETICS PROGRAM

```
      DIMENSION AK(34),C(30),CPDNAM(30),D(34),DATE(2),
      HEADER(10)
      DIMENSION ISS(16),JRE(34,4),JSS(16,34),JTENTY(8),
      TBLCPD(8)
      DIMENSION CHOLD(8,50),TIME(50)
      DIMENSION TBLH(8),DL(34),EQUAT(6),PROBLM(12)
      MXAPP=33
      MXCPDS = 30
      IQ79=0
      MXR = 34
      MXSTST = 16
      MXTBNT = 8
      READ (7,7000) BL
 7000 FORMAT (A4)
      READ (7,8009) DAMP,SCALEF
 8009 FORMAT (2E8.4)
    5 DO 10 N = 1, MXR
      DO 10 J = 1, 4
   10 JRE (N,J) = 0
   12 DO 15 J = 1, MXSTST
   13 ISS (J) = 0
   14 DO 15 I = 1,MXAPP
   15 JSS (J,I) = 0
      DO 17 J = 1, MXTBNT
   17 TBLH (J) = BL
   20 READ (7,8000) DATE,HEADER
 8000 FORMAT (1X,12A4)
   25 WRITE (5,9000) DATE,HEADER
 9000 FORMAT (12A4)
   30 READ (7,8010) NCPDS, NSS, NR, NRCAT, NCPCAT
      WRITE (5,6995)
 6995 FORMAT (1H2)
      WRITE (5,8010) NCPDS,NSS,NR,NRCAT,NCPCAT
 8010 FORMAT (14(I4))
   31 IF (NCPDS-MXCPDS) 35,35,32
   32 NCPDS = MXCPDS
   33 WRITE (5,9001)
 9001 FORMAT (' ', ' TOO MANY COMPOUNDS')
   35 IF (NSS-MXSTST) 39,39,36
```

```
   36 NSS = MXSTST
   37 WRITE (5,9002)
 9002 FORMAT (' ',' TOO MANY SS COMPOUNDS')
   39 IF (NR-MXR) 45,45,40
   40 NR = MXR
   41 WRITE (5,9003)
 9003 FORMAT (' ',' TOO MANY REACTIONS')
   45 READ (7,8020) (CPDNAM (K), K = 1, NCPDS)
 8020 FORMAT (7(4X,A4),/,7(4X,A4))
      WRITE (5,8020) (CPDNAM(K),K=1,NCPDS)
   50 DO 77 N=1,NR
   52 READ (7,8010) (JRE(N,I), I=1,4)
   53 IF (NSS) 77,77,54
   54 DO 75 I = 1,4
   55 IF (JRE (N,I)) 75,75,56
   56 IF (JRE (N,I) - NSS) 58,58,75
   58 J = IABS (JRE (N,I))
   60 IS = ISS (J) +1
   61 ISS (J) = IS
   63 IF (IS - MXAPP) 67,67,64
   64 ISS (J) = ISS (J) - 1
   65 WRITE (5,9005) CPDNAM (J)
 9005 FORMAT (' ',' TOO MANY APPEARANCES OF ', A4)
   66 IS = MXAPP
   67 JSS (J,IS) = N
   68 JRE (N,I) = -JRE (N,I)
   70 IF (I-3) 72,75,75
   72 JSS (J,IS) = -N
   75 CONTINUE
   77 CONTINUE
   80 NSSI = NSS + 1
   85 IF (NSS) 110,110,100
  100 WRITE (5,9010) (CPDNAM(K),K = 1,NSS)
 9010 FORMAT (' ', 3X, ' STEADY STATE INTERMEDIATES-',1X,
     17 (A4,2X))
  110 WRITE (5,9020) (CPDNAM(K), K = NSSI, NCPDS)
 9020 FORMAT (' ',' REACTANTS AND PRODUCTS-',5X,7(A4,2X)/31X,
     17(A4,2X))
  120  DO 200 N = 1,NR
       JJ = IABS (JRE (N,1))
       EQUAT(1) = CPDNAM (JJ)
  130 IF (JRE (N,2)) 140,150,140
  140 JJ = IABS (JRE (N,2))
       EQUAT(3) = CPDNAM (JJ)
       GO TO 160
  150 EQUAT(2) = BL
       EQUAT(3) = BL
  160 JJ = IABS (JRE(N,3))
       EQUAT(4) = CPDNAM (JJ)
       IF (JRE (N,4)) 170,180,170
  170 JJ = IABS (JRE (N,4))
```

```
      EQUAT(6) = CPDNAM (JJ)
      GO TO 182
  180 EQUAT(5) = BL
      EQUAT(6) = BL
  182 IF (JRE (N,2) .EQ. 0) GO TO 184
      IF (JRE (N,4) .EQ. 0) GO TO 188
      WRITE (5,9030) N,EQUAT(1), EQUAT(3), EQUAT(4), EQUAT(6)
      GO TO 200
 9030 FORMAT (' ', I3, 1X, A4, ' + ', A4, 2X, '=',2X, A4,
     1' + ', A4)
  184 IF (JRE (N,4) .EQ. 0) GO TO 186
      WRITE (5,9031) N, EQUAT(1), EQUAT(3), EQUAT(4),
     1EQUAT(6)
      GO TO 200
 9031 FORMAT (' ', I3, 1X, A4, 3X, A4, 2X, '=', 2X, A4,
     1' + ', A4)
  186 WRITE (5,9032) N, EQUAT(1), EQUAT(3), EQUAT(4),
     1EQUAT(6)
      GO TO 200
 9032 FORMAT (' ', I3, 1X, A4, 3X, A4, 2X, '=', 2X, A4, 3X,
     1A4)
  188 WRITE (5,9033) N, EQUAT(1), EQUAT(3), EQUAT(4), EQUAT
     1(6)
 9033 FORMAT (' ', I3, 1X, A4, ' + ', A4, 2X, '=',2X, A4,
     13X, A4)
  200 CONTINUE
  230 IF (NCPCAT * NRCAT) 240,240,235
  235 WRITE (5,9045) NRCAT, CPDNAM (NCPCAT)
 9045 FORMAT (' ', 'REACTION ', I2, 1X, 'IS CATALYZED BY',
     1A4)
  240 READ (7,8010) NPROB,NREPSS
  260 DO 900 NPRB = 1, NPROB
  270 READ (7,8000) PROBLM
  280 READ (7,8050) (AK (N), N = 1,NR)
 8050 FORMAT (7E10.5)
  285 WRITE (5,9000) HEADER, DATE
      WRITE (5,6995)
  290 WRITE (5,9060) PROBLM
 9060 FORMAT (' ', ' ', 12A4)
  300 READ (7,8060) NP,NI,DT,T,IWRITE,NTENT
  301 WRITE (5,8060) NP,NI,DT,T,IWRITE,NTENT
 8060 FORMAT (I5,I4,2E10.5,I3,I4)
  305 IF (NTENT-MXTENT) 307,307,306
  306 NTENT = MXTENT
  307 READ (7,8010) (JTENTY (I), I = 1, NTENT)
      WRITE (5,6995)
  310 WRITE (5,9070)  DT, (N, AK (N), N = 1, NR)
 9070 FORMAT (' DT = ',1PE13.5,/,' RATE CONSTANTS-',1X,
     15(I2,1X,E11.5,3X)/17X,5(I2,1X,E11.5,3X),/,17X,
     25(I2,1X,E11.5,3X),/,17X,5(I2,1X,E11.5,3X),/,17X,
     35(I2,1X,E11.5,3X),/,17X,5(I2,1X,E11.5,3X),/,17X,
     45(I2,1X,E11.5,3X))
```

```
  315 READ (7,8050) (C(I), I = 1, NCPDS)
      READ(7,8050) CSSTOT
  317 DO 319 I = 1, NTENT
  318 J = JTENTY (I)
  319 TBLH (I) = CPDNAM (J)
      WRITE (5,6996)
 6996 FORMAT (1H1)
  320 WRITE (5,9080)  (TBLH (I), I = 1, NTENT)
 9080 FORMAT (' ',/, 6X, 'TIME', 10X, 8(A4, 9X))
  322 IF (NSS) 332,332,323
  323 DO 326 I = 1, NSS
  324 IF (C(I)) 325,325,326
  325 C(I) = 1.0E-20
  326 CONTINUE
  332 DO 334 I = 1, NTENT
  333 J = JTENTY (I)
  334 TBLCPD (I) = C(J)
  340 WRITE (5,9090) T, (TBLCPD (I), I = 1, NTENT)
 9090 FORMAT (' ', 1P9E13.4)
      DO 350 N = 1, NR
  345 DL (N) = 0
  350 AK (N) = AK (N) * DT
  360 DO 850 IP = 1, NP
  370 DO 800 IT = 1, NI
  375 IF (NSS) 580,580,380
  380 DO 550 IREP = 1,NREPSS
  390 DO 420 N = 1, NR
      N1 = IABS (JRE (N,1))
      N2 = IABS (JRE (N,2))
      IF (N2) 400,400,410
  400 D(N) = AK(N) * C(N1)
      GO TO 420
  410 D(N) = AK(N) * C(N1) * C(N2)
  420 CONTINUE
      ITEST = 0
  430 DO 530 IS = 1, NSS
      IST = ISS(IS)
      XNUM = 0.
      DEN = 0.
  440 DO 470 JS = 1, IST
  445 KS = JSS (IS, JS)
  446 IF (KS) 460,470,450
  450 XNUM = XNUM + D(KS)
  452 GO TO 470
  460 KS = -KS
  465 DEN = DEN + D(KS)
  470 CONTINUE
      IF (DEN) 472,475,472
  472 F = XNUM/DEN
      IF (F) 477,475,477
  475 F = 1.
```

```
      GO TO 488
  477 IF (F - 1.)480,488,484
  480 F = DAMP/F + 1.-DAMP
      F = 1./F
      GO TO 488
  484 F = F*DAMP + 1. -DAMP
  488 C(IS) = C(IS) * F
      FW = F - 1.
  490 IF (IWRITE)510,510,500
  500 WRITE (5,9100)IP,IT,IREP,XNUM,DEN,FW,
     1(CPDNAM(I),C(I),I=1,NSS)
 9100 FORMAT (´ ´,´PRINT INTERVAL´,I3,2X,´ITERATION´,I3,2X,
     1´SS REPEAT´,I3,2X,´NUMERATOR´,1PE12.5,2X,
     2´DENOMINATOR´E12.5,2X,´PER CENT CORRN.´,2PF10.3,/,1X,
     36HCONCS.,1X,A4,1PE12.5,2X,A4,E12.5,2X,A4,E12.5,2X,A4,
     4E12.5,2X,A4,E12.5,/A4,1PE12.5,2X,A4,E12.5,2X,A4,E12.5,
     52X,A4,E12.5)
  510 IF (ABS(FW) - .005)530,530,520
  520 ITEST = 1
  530 CONTINUE
  531 IF (CSSTOT)540,540,532
  532 CS = 0.
      DO 533 I = 1, NSS
  533 CS = CS + C(I)
      F = CSSTOT/CS
      DO 537 I = 1, NSS
  537 C(I) = C(I) * F
  540 IF (ITEST) 550,560,550
  550 CONTINUE
  553 WRITE (5,9110) NREPSS
 9110 FORMAT (´ ´,´STEADY STATE CALCULATION DID NOT
     1CONVERGE´,´ IN´,I2,1X,´ITERATIONS´)
  555 WRITE (5,9100) IP,IT,IREP,XNUM,DEN,FW,
     1(CPDNAM(I),C(I),I=1,NCPDS)
      GO TO 900
  560 IF (IP * IT - 1) 580,570,580
  570 DO 575 I = 1, NTENT
  572 J = JTENTY(I)
  575 TBLCPD(I) = C(J)
  576 WRITE (5,9090) T,(TBLCPD(I),I = 1,NTENT)
  580 CONTINUE
  585 DO 620 N = 1, NR
      N1 = IABS(JRE(N,1))
      N2 = IABS(JRE(N,2))
  590 IF (N2) 600,600,610
  600 D(N) = AK(N) * C(N1)
      GO TO 620
  610 D(N) = AK(N) * C(N1) * C(N2)
  620 CONTINUE
  625 IF (NCPCAT * NRCAT) 630,630,627
  627 D(NRCAT) = D(NRCAT) * C(NCPCAT)
  630 DO 638 N = 1, NR
```

```
  631 IF (DL(N)) 636,636,632
  632 DLAST = D(N)
  633 D(N) = 1.5 * D(N) - 0.5 * DL(N)
  634 DL(N) = DLAST
  635 GO TO 638
  636 DL(N) = D(N)
  638 CONTINUE
  640 DO 680 N = 1, NR
  642 DO 680 I = 1,4
  644 IF (JRE(N,I)) 680,680,645
  645 II = JRE(N,I)
  650 IF (I - 3) 655,665,665
  655 C(II) = C(II) - D(N)
  660 GO TO 680
  665 C(II) = C(II) + D(N)
  680 CONTINUE
  681 NGCHK = 0
  682 DO 685 I = 1, NCPDS
  683 IF (C(I)) 684,685,685
  684 NGCHK = NGCHK + 1
  685 CONTINUE
  690 IF (NGCHK) 750,750,700
  700 WRITE (5,9120) IT,(C(I),I=1,NCPDS)
 9120 FORMAT (´ ´,´ NEGATIVE CONCS.-(INTERVAL´,I3,1X,´ )
     1C-ARRAY´,1P6E14.5,/,40X,6E14.5)
  710 WRITE (5,9130) (D(I), I = 1, NR)
 9130 FORMAT (´ ´,33X,´D-ARRAY´,1PE14.5,/,40X,6E14.5)
  720 GO TO 900
  750 T = T + DT
  800 CONTINUE
  805 DO 807 I = 1, NTENT
  806 J = JTENTY(I)
  807 TBLCPD(I) = C(J)*SCALEF
  810 WRITE (5,9090) T,(TBLCPD(I),I=1,NTENT)
  815 TIME(IP) = T
  820 DO 830 KK = 1,NTENT
  830 CHOLD(KK,IP) = TBLCPD(KK)
  850 CONTINUE
 9095 FORMAT (´ ´, 1P8E13.4)
  860 WRITE (8,9095) CHOLD
  900 CONTINUE
      END
```

# APPENDIX V

## OUTPUT OF COMPUTER SIMULATION PROGRAM

### Fortran Data File

```
0.7,1.0
                    PROPANE RADIOLYSIS
 20,9,25,0,0
   H*       H.       CH3.     ET*      C2H5     C3H7     PR*
   C3H5     C3H8*    H2       CH4      C2H6     C4HX     C5HY
   C6HZ     C2H4     C3H6     W        POLY     C3H8
 20,0,9,0
 20,0,6,1
 20,0,10,17
 20,0,11,16
 20,0,4,3
 20,0,7,2
 7,0,8,10
 9,0,3,5
 4,20,12,6
 1,20,10,6
 1,20,2,20
 2,20,10,6
 3,20,11,6
 5,20,12,6
 3,3,12,0
 5,5,12,16
 5,5,13,0
 3,6,13,0
 5,6,14,0
 6,6,15,0
 6,6,20,17
 8,6,17,17
 16,18,19,0
 17,18,19,0
 20,18,19,10
 1,400
PROBLEM ONE
 3.9E-9,4.35E-9,6.52E-9,3.24E-9,4.76E-9,7.8E-10,1.0E12
 9.0E7,1E12,1.1E9,1.0E9,9.0E4,1.0E2,1.0E2
 2.5E10,1E10,1.4E10,1.2E10,1.60E10,3.4E9,2.00E9
 2E9,5.0E3,1.0E4,7.50E-4
 50,20,1E1,0.0,0,8
 10,11,12,13,14,15,16,17
 1.0E-20,1.0E-20,1.0E-20,1.0E-20,1.0E-20,1.0E-20,1E-20
 1.0E-20,1.0E-20,1.0E-20,1.0E-20,1.0E-20,1.0E-20,1E-20
 1E-20,1E-20,1E-20,1,1E-20,5.3BE-3
 0,0,0,0,0
```

# Output of Computer Simulation Program:

## Mechanism and System Parameters

```
                    PROPANE RADIOLYSIS

 20   9  25   0   0
   H*       H.       CH3.     ET*      C2H5     C3H7     PR*
   C3H5     C3B*     H2       CH4      C2H6     C4HX     C5HY
   C6HZ     C2H4     C3H6     W        POLY     C3H8
    STEADY STATE INTERMEDIATES- H*    H.    CH3.  ET*   C2H5  C3H7  PR*
    STEADY STATE INTERMEDIATES- C3H5  C3B*
REACTANTS AND PRODUCTS-      H2    CH4   C2H6  C4HX  C5HY  C6HZ  C2H4
                               C3H6  W     POLY  C3H8
  1 C3H8          =  C3B*
  2 C3H8          =  C3H7 + H*
  3 C3H8          =  H2   + C3H6
  4 C3H8          =  CH4  + C2H4
  5 C3H8          =  ET*  + CH3.
  6 C3H8          =  PR*  + H.
  7 PR*           =  C3H5 + H2
  8 C3B*          =  CH3. + C2H5
  9 ET*  + C3H8   =  C2H6 + C3H7
 10 H*   + C3H8   =  H2   + C3H7
 11 H*   + C3H8   =  H.   + C3H8
 12 H.   + C3H8   =  H2   + C3H7
 13 CH3. + C3H8   =  CH4  + C3H7
 14 C2H5 + C3H8   =  C2H6 + C3H7
 15 CH3. + CH3.   =  C2H6
 16 C2H5 + C2H5   =  C2H6 + C2H4
 17 C2H5 + C2H5   =  C4HX
 18 CH3. + C3H7   =  C4HX
 19 C2H5 + C3H7   =  C5HY
 20 C3H7 + C3H7   =  C6HZ
 21 C3H7 + C3H7   =  C3H8 + C3H6
 22 C3H5 + C3H7   =  C3H6 + C3H6
 23 C2H4 + W      =  POLY
 24 C3H6 + W      =  POLY
 25 C3H8 + W      =  POLY + H2
       PROPANE RADIOLYSIS

 PROBLEM ONE
  50  20.10000E+02.00000E+01  0  8

DT =   1.00000E+01
RATE CONSTANTS-  1 3.90000E-09    2 4.35000E-09    3 6.52000E-09    4 3.24000E-09    5 4.76000E-09
                 6 7.80000E-10    7 1.00000E+12    8 9.00000E+07    9 1.00000E+12   10 1.10000E+09
                11 1.00000E+09   12 9.00000E+04   13 1.00000E+02   14 1.00000E+02   15 2.50000E+10
                16 1.00000E+10   17 1.40000E+10   18 1.20000E+10   19 1.60000E+10   20 3.40000E+09
                21 2.00000E+09   22 2.00000E+09   23 5.00000E+03   24 1.00000E+04   25 7.50000E-04
```

Output of Computer Simulation Program: Product Concentration (moles/liter) versus Time (sec)

| TIME | H2 | CH4 | C2H6 | C4H10 | C5H12 | C6H14 | C2H4 | C3H6 |
|---|---|---|---|---|---|---|---|---|
| 0.0000E+00 | 1.0000E-20 | 1.0000E-20 | 1.0000E-20 | 1.0000E-20 | 1.0000E-20 | 1.0000E-20 | 1.0000E-20 | 1.0000E-20 |
| 0.0000E+00 | 1.0000E-20 | 1.0000E-20 | 1.0000E-20 | 1.0000E-20 | 1.0000E-20 | 1.0000E-20 | 1.0000E-20 | 1.0000E-20 |
| 2.0000E+02 | 2.1436E-08 | 5.5761E-09 | 8.2256E-09 | 3.7141E-09 | 2.2781E-09 | 3.7375E-09 | 3.6773E-10 | 3.6834E-10 |
| 4.0000E+02 | 4.2854E-08 | 1.1152E-08 | 1.6451E-08 | 7.4281E-09 | 4.5561E-09 | 7.4749E-09 | 3.6860E-10 | 3.8411E-10 |
| 6.0000E+02 | 6.4253E-08 | 1.6728E-08 | 2.4677E-08 | 1.1142E-08 | 6.8341E-09 | 1.1212E-08 | 3.6944E-10 | 4.0749E-10 |
| 8.0000E+02 | 8.5634E-08 | 2.2304E-08 | 3.2902E-08 | 1.4856E-08 | 9.1121E-09 | 1.4950E-08 | 3.7028E-10 | 4.3501E-10 |
| 1.0000E+03 | 1.0700E-07 | 2.7880E-08 | 4.1127E-08 | 1.8570E-08 | 1.1390E-08 | 1.8687E-08 | 3.7112E-10 | 4.6313E-10 |
| 1.2000E+03 | 1.2834E-07 | 3.3456E-08 | 4.9352E-08 | 2.2284E-08 | 1.3668E-08 | 2.2425E-08 | 3.7197E-10 | 4.8890E-10 |
| 1.4000E+03 | 1.4967E-07 | 3.9032E-08 | 5.7578E-08 | 2.5998E-08 | 1.5946E-08 | 2.6162E-08 | 3.7282E-10 | 5.1050E-10 |
| 1.6000E+03 | 1.7098E-07 | 4.4608E-08 | 6.5803E-08 | 2.9712E-08 | 1.8224E-08 | 2.9899E-08 | 3.7367E-10 | 5.2726E-10 |
| 1.8000E+03 | 1.9226E-07 | 5.0183E-08 | 7.4028E-08 | 3.3425E-08 | 2.0502E-08 | 3.3636E-08 | 3.7452E-10 | 5.3943E-10 |
| 2.0000E+03 | 2.1354E-07 | 5.5759E-08 | 8.2253E-08 | 3.7139E-08 | 2.2780E-08 | 3.7374E-08 | 3.7538E-10 | 5.4783E-10 |
| 2.2000E+03 | 2.3479E-07 | 6.1335E-08 | 9.0478E-08 | 4.0853E-08 | 2.5058E-08 | 4.1111E-08 | 3.7624E-10 | 5.5343E-10 |
| 2.4000E+03 | 2.5602E-07 | 6.6910E-08 | 9.8703E-08 | 4.4567E-08 | 2.7335E-08 | 4.4848E-08 | 3.7711E-10 | 5.5716E-10 |
| 2.6000E+03 | 2.7724E-07 | 7.2486E-08 | 1.0693E-07 | 4.8280E-08 | 2.9613E-08 | 4.8585E-08 | 3.7797E-10 | 5.5974E-10 |
| 2.8000E+03 | 2.9844E-07 | 7.8061E-08 | 1.1515E-07 | 5.1994E-08 | 3.1891E-08 | 5.2322E-08 | 3.7885E-10 | 5.6167E-10 |
| 3.0000E+03 | 3.1962E-07 | 8.3637E-08 | 1.2338E-07 | 5.5708E-08 | 3.4169E-08 | 5.6060E-08 | 3.7972E-10 | 5.6326E-10 |
| 3.2000E+03 | 3.4078E-07 | 8.9212E-08 | 1.3160E-07 | 5.9422E-08 | 3.6447E-08 | 5.9797E-08 | 3.8060E-10 | 5.6459E-10 |
| 3.4000E+03 | 3.6192E-07 | 9.4788E-08 | 1.3983E-07 | 6.3135E-08 | 3.8725E-08 | 6.3534E-08 | 3.8148E-10 | 5.6605E-10 |
| 3.6000E+03 | 3.8305E-07 | 1.0036E-07 | 1.4805E-07 | 6.6849E-08 | 4.1002E-08 | 6.7271E-08 | 3.8236E-10 | 5.6738E-10 |
| 3.8000E+03 | 4.0416E-07 | 1.0594E-07 | 1.5628E-07 | 7.0563E-08 | 4.3280E-08 | 7.1008E-08 | 3.8325E-10 | 5.6871E-10 |
| 4.0000E+03 | 4.2525E-07 | 1.1151E-07 | 1.6450E-07 | 7.4276E-08 | 4.5558E-08 | 7.4745E-08 | 3.8414E-10 | 5.7003E-10 |
| 4.2000E+03 | 4.4632E-07 | 1.1709E-07 | 1.7273E-07 | 7.7990E-08 | 4.7836E-08 | 7.8481E-08 | 3.8504E-10 | 5.7136E-10 |
| 4.4000E+03 | 4.6737E-07 | 1.2266E-07 | 1.8095E-07 | 8.1703E-08 | 5.0113E-08 | 8.2218E-08 | 3.8593E-10 | 5.7270E-10 |
| 4.6000E+03 | 4.8840E-07 | 1.2824E-07 | 1.8918E-07 | 8.5417E-08 | 5.2391E-08 | 8.5955E-08 | 3.8684E-10 | 5.7403E-10 |
| 4.8000E+03 | 5.0942E-07 | 1.3381E-07 | 1.9740E-07 | 8.9130E-08 | 5.4669E-08 | 8.9692E-08 | 3.8774E-10 | 5.7536E-10 |
| 5.0000E+03 | 5.3042E-07 | 1.3939E-07 | 2.0562E-07 | 9.2844E-08 | 5.6946E-08 | 9.3429E-08 | 3.8865E-10 | 5.7673E-10 |
| 5.2000E+03 | 5.5140E-07 | 1.4496E-07 | 2.1385E-07 | 9.6557E-08 | 5.9224E-08 | 9.7166E-08 | 3.8956E-10 | 5.7808E-10 |
| 5.4000E+03 | 5.7236E-07 | 1.5054E-07 | 2.2207E-07 | 1.0027E-07 | 6.1502E-08 | 1.0090E-07 | 3.9048E-10 | 5.7944E-10 |
| 5.6000E+03 | 5.9331E-07 | 1.5611E-07 | 2.3030E-07 | 1.0398E-07 | 6.3779E-08 | 1.0464E-07 | 3.9140E-10 | 5.8080E-10 |
| 5.8000E+03 | 6.1423E-07 | 1.6169E-07 | 2.3852E-07 | 1.0770E-07 | 6.6057E-08 | 1.0838E-07 | 3.9232E-10 | 5.8217E-10 |
| 6.0000E+03 | 6.3514E-07 | 1.6726E-07 | 2.4674E-07 | 1.1141E-07 | 6.8335E-08 | 1.1211E-07 | 3.9325E-10 | 5.8355E-10 |
| 6.2000E+03 | 6.5603E-07 | 1.7284E-07 | 2.5497E-07 | 1.1512E-07 | 7.0612E-08 | 1.1585E-07 | 3.9418E-10 | 5.8493E-10 |
| 6.4000E+03 | 6.7690E-07 | 1.7841E-07 | 2.6319E-07 | 1.1884E-07 | 7.2890E-08 | 1.1959E-07 | 3.9511E-10 | 5.8631E-10 |
| 6.6000E+03 | 6.9776E-07 | 1.8399E-07 | 2.7141E-07 | 1.2255E-07 | 7.5167E-08 | 1.2332E-07 | 3.9605E-10 | 5.8770E-10 |
| 6.8000E+03 | 7.1859E-07 | 1.8956E-07 | 2.7964E-07 | 1.2626E-07 | 7.7445E-08 | 1.2706E-07 | 3.9698E-10 | 5.8910E-10 |
| 7.0000E+03 | 7.3941E-07 | 1.9514E-07 | 2.8786E-07 | 1.2998E-07 | 7.9722E-08 | 1.3080E-07 | 3.9793E-10 | 5.9050E-10 |
| 7.2000E+03 | 7.6021E-07 | 2.0071E-07 | 2.9608E-07 | 1.3369E-07 | 8.2000E-08 | 1.3453E-07 | 3.9888E-10 | 5.9191E-10 |
| 7.4000E+03 | 7.8100E-07 | 2.0629E-07 | 3.0431E-07 | 1.3740E-07 | 8.4277E-08 | 1.3827E-07 | 3.9983E-10 | 5.9332E-10 |
| 7.6000E+03 | 8.0176E-07 | 2.1186E-07 | 3.1253E-07 | 1.4112E-07 | 8.6555E-08 | 1.4200E-07 | 4.0079E-10 | 5.9474E-10 |
| 7.8000E+03 | 8.2251E-07 | 2.1743E-07 | 3.2076E-07 | 1.4483E-07 | 8.8832E-08 | 1.4574E-07 | 4.0175E-10 | 5.9617E-10 |
| 8.0000E+03 | 8.4324E-07 | 2.2301E-07 | 3.2898E-07 | 1.4854E-07 | 9.1110E-08 | 1.4948E-07 | 4.0271E-10 | 5.9760E-10 |
| 8.2000E+03 | 8.6395E-07 | 2.2858E-07 | 3.3720E-07 | 1.5225E-07 | 9.3387E-08 | 1.5321E-07 | 4.0368E-10 | 5.9904E-10 |
| 8.4000E+03 | 8.8464E-07 | 2.3416E-07 | 3.4542E-07 | 1.5597E-07 | 9.5665E-08 | 1.5695E-07 | 4.0465E-10 | 6.0048E-10 |
| 8.6000E+03 | 9.0532E-07 | 2.3973E-07 | 3.5365E-07 | 1.5968E-07 | 9.7942E-08 | 1.6069E-07 | 4.0563E-10 | 6.0193E-10 |
| 8.8000E+03 | 9.2598E-07 | 2.4531E-07 | 3.6187E-07 | 1.6339E-07 | 1.0022E-07 | 1.6442E-07 | 4.0661E-10 | 6.0338E-10 |
| 9.0000E+03 | 9.4662E-07 | 2.5088E-07 | 3.7009E-07 | 1.6711E-07 | 1.0250E-07 | 1.6816E-07 | 4.0759E-10 | 6.0484E-10 |
| 9.2000E+03 | 9.6724E-07 | 2.5645E-07 | 3.7832E-07 | 1.7082E-07 | 1.0477E-07 | 1.7190E-07 | 4.0858E-10 | 6.0630E-10 |
| 9.4000E+03 | 9.8784E-07 | 2.6203E-07 | 3.8654E-07 | 1.7453E-07 | 1.0705E-07 | 1.7563E-07 | 4.0957E-10 | 6.0777E-10 |
| 9.6000E+03 | 1.0084E-06 | 2.6760E-07 | 3.9476E-07 | 1.7825E-07 | 1.0933E-07 | 1.7937E-07 | 4.1057E-10 | 6.0925E-10 |
| 9.8000E+03 | 1.0290E-06 | 2.7318E-07 | 4.0298E-07 | 1.8196E-07 | 1.1161E-07 | 1.8310E-07 | 4.1157E-10 | 6.1074E-10 |
| 1.0000E+04 | 1.0496E-06 | 2.7875E-07 | 4.1121E-07 | 1.8567E-07 | 1.1388E-07 | 1.8684E-07 | 4.1257E-10 | 6.1222E-10 |

## Fortran Data File

```
0.7,1.0
                PROPANE - OXYGEN SYSTEM
29,10,32,0,0
  H*      H.      PR*     AL.     IP.     NP.     C3H*
  IPOD    NPOD    ALOD    HO2.    IPO2    NPO2    ALO2
  IPO.    NPO.    ALO.    H2      H2O2    C12P    H2O
  PK      IPOH    PA      NPOH    ALA     ALOH    O2
  C3H8
29,0,7,0
29,0,5,1
29,0,6,1
29,0,3,2
3,0,4,18
7,0,20,0
7,28,24,21
7,28,29,28
1,28,11,0
1,29,18,5
1,29,18,6
1,29,2,29
2,29,18,5
5,28,12,0
6,28,13,0
4,28,14,0
2,28,11,0
12,12,8,28
8,0,15,15
13,13,9,28
9,0,16,16
14,14,10,28
10,0,17,17
11,11,19,28
15,15,22,23
15,16,22,25
15,16,24,23
16,16,24,25
17,17,26,27
15,11,22,19
16,11,24,19
17,11,26,19
1.400
PROBLEM ONE
 4.54E-9,6.40E-9,1.93E-9,8.86E-10,1.00E12,9.00E7,3.25E10
 3.00E10,1.50E10,1.00E9,1.00E8,1.00E9,8.20E4,4.63E10
 2.00E10,1.00E10,3.00E11,1.00E10,1.00E12,1.00E9,1.00E12
 6.00E10,1.00E12,2.00E9,3.00E10,1.00E9,1.00E9,1.00E8
 1.2E10,9.4E8,6.4E8,4.0E9
 50,10,0.200,0.0,0,8
 18,21,22,23,24,25,26,27
 1.0E-16,1.0E-16,1.0E-16,1.0E-16,1.0E-16,1.0E-16,1.0E-162
 1.0E-16,1.0E-16,1.0E-16,1.0E-16,1.0E-16,1.0E-16,1.0E-16
 1.0E-16,1.0E-16,1.0E-16,1.0E-16,1.0E-16,1.0E-16,1.0E-16
 1.0E-16,1.0E-16,1.0E-16,1.0E-16,1.0E-16,1.0E-16,5.38E-4
 5.38E-3
 0,0,0,0,0
```

# Output of Computer Simulation Program:

## Mechanism and System Parameters

```
                PROPANE - OXYGEN SYSTEM

 29  10  32   0   0
   H*      H.      PR*     AL.     IP.     NP.     C3H*
   IPOD    NPOD    ALOD    HO2.    IPO2    NPO2    ALO2
   IPO.    NPO.    ALO.    H2      H2O2    C12P    H2O
   PK      IPOH    PA      NPOH    ALA     ALOH    O2
   C3H8
    STEADY STATE INTERMEDIATES- H*    H.    PR*   AL.   IP.   NP.   C3H*
    STEADY STATE INTERMEDIATES- IPOD  NPOD  ALOD
REACTANTS AND PRODUCTS-      HO2. IPO2 NPO2 ALO2 IPO. NPO. ALO.
                               H2   H2O2 C12P H2O  PK   IPOH PA
REACTANTS AND PRODUCTS-      NPOH ALA  ALOH O2   C3H8
  1 C3H8          =  C3H*
  2 C3H8          =  IP.  + H*
  3 C3H8          =  NP.  + H*
  4 C3H8          =  PR*  + H.
  5 PR*           =  AL.  + H2
  6 C3H*          =  C12P
  7 C3H* + O2     =  PA   + H2O
  8 C3H* + O2     =  C3H8 + O2
  9 H*   + O2     =  HO2.
 10 H*   + C3H8   =  H2    + IP.
 11 H*   + C3H8   =  H2    + NP.
 12 H*   + C3H8   =  H.    + C3H8
 13 H.   + C3H8   =  H2    + IP.
 14 IP.  + O2     =  IPO2
 15 NP.  + O2     =  NPO2
 16 AL.  + O2     =  ALO2
 17 H.   + O2     =  HO2.
 18 IPO2 + IPO2   =  IPOD  + O2
 19 IPOD          =  IPO.  + IPO.
 20 NPO2 + NPO2   =  NPOD  + O2
 21 NPOD          =  NPO.  + NPO.
 22 ALO2 + ALO2   =  ALOD  + O2
 23 ALOD          =  ALO.  + ALO.
 24 HO2. + HO2.   =  H2O2  + O2
 25 IPO. + IPO.   =  PK    + IPOH
 26 IPO. + NPO.   =  PK    + NPOH
 27 IPO. + NPO.   =  PA    + IPOH
 28 NPO. + NPO.   =  PA    + NPOH
 29 ALO. + ALO.   =  ALA   + ALOH
 30 IPO. + HO2.   =  PK    + H2O2
 31 NPO. + HO2.   =  PA    + H2O2
 32 ALO. + HO2.   =  ALA   + H2O2
      PROPANE - OXYGEN SYSTEM

 PROBLEM ONE
  50  10.20000E+00.00000E+01  0   8

DT =   2.00000E-01
RATE CONSTANTS-  1 4.54000E-09   2 6.40000E-09   3 1.93000E-09   4 8.86000E-10   5 1.00000E+12
                 6 9.00000E+07   7 3.25000E+10   8 3.00000E+10   9 1.50000E+10  10 1.00000E+09
                11 1.00000E+08  12 1.00000E+09  13 8.20000E+04  14 4.63000E+10  15 2.00000E+10
                16 1.00000E+10  17 3.00000E+11  18 1.00000E+10  19 1.00000E+12  20 1.00000E+09
                21 1.00000E+12  22 6.00000E+10  23 1.00000E+12  24 2.00000E+09  25 3.00000E+10
                26 1.00000E+09  27 1.00000E+09  28 1.00000E+08  29 1.20000E+10  30 9.40000E+08
                31 6.40000E+08  32 4.00000E+09
```

Output of Computer Simulation Program: Product Concentration (moles/liter) versus Time (sec)

| TIME | H2 | H2O | PK | IPOH | PA | NPOH | ALA | ALOH |
|---|---|---|---|---|---|---|---|---|
| 0.0000E+00 | 1.0000E-16 | 1.0000E-16 | 1.0000E-16 | 1.0000E-16 | 1.0000E-16 | 1.0000E-16 | 1.0000E-16 | 1.0000E-16 |
| 0.0000E+00 | 1.0000E-16 | 1.0000E-16 | 1.0000E-16 | 1.0000E-16 | 1.0000E-16 | 1.0000E-16 | 1.0000E-16 | 1.0000E-16 |
| 2.0000E+00 | 3.6921E-11 | 6.9095E-12 | 1.2050E-11 | 1.1133E-11 | 6.9254E-12 | 6.2569E-15 | 4.4480E-13 | 4.9142E-14 |
| 4.0000E+00 | 7.3841E-11 | 1.3818E-11 | 5.8252E-11 | 5.3680E-11 | 1.4172E-11 | 1.2746E-13 | 4.6120E-12 | 8.5153E-13 |
| 6.0000E+00 | 1.1076E-10 | 2.0728E-11 | 1.0730E-10 | 9.8425E-11 | 2.2412E-11 | 5.8178E-13 | 1.1534E-11 | 2.3871E-12 |
| 8.0000E+00 | 1.4768E-10 | 2.7637E-11 | 1.5645E-10 | 1.4320E-10 | 3.2259E-11 | 1.5836E-12 | 1.9125E-11 | 4.1226E-12 |
| 1.0000E+01 | 1.8460E-10 | 3.4546E-11 | 2.0558E-10 | 1.8800E-10 | 4.3968E-11 | 3.2762E-12 | 2.6820E-11 | 5.9206E-12 |
| 1.2000E+01 | 2.2152E-10 | 4.1455E-11 | 2.5469E-10 | 2.3283E-10 | 5.7646E-11 | 5.7137E-12 | 3.4517E-11 | 7.7011E-12 |
| 1.4000E+01 | 2.5844E-10 | 4.8364E-11 | 3.0375E-10 | 2.7769E-10 | 7.3135E-11 | 8.8768E-12 | 4.2202E-11 | 9.5149E-12 |
| 1.6000E+01 | 2.9537E-10 | 5.5274E-11 | 3.5277E-10 | 3.2256E-10 | 9.0207E-11 | 1.2699E-11 | 4.9875E-11 | 1.1343E-11 |
| 1.8000E+01 | 3.3229E-10 | 6.2183E-11 | 4.0175E-10 | 3.6744E-10 | 1.0861E-10 | 1.7094E-11 | 5.7540E-11 | 1.3183E-11 |
| 2.0000E+01 | 3.6921E-10 | 6.9092E-11 | 4.5071E-10 | 4.1233E-10 | 1.2810E-10 | 2.1970E-11 | 6.5198E-11 | 1.5035E-11 |
| 2.2000E+01 | 4.0613E-10 | 7.6001E-11 | 4.9964E-10 | 4.5723E-10 | 1.4847E-10 | 2.7239E-11 | 7.2851E-11 | 1.6895E-11 |
| 2.4000E+01 | 4.4305E-10 | 8.2910E-11 | 5.4855E-10 | 5.0213E-10 | 1.6953E-10 | 3.2825E-11 | 8.0501E-11 | 1.8763E-11 |
| 2.6000E+01 | 4.7997E-10 | 8.9820E-11 | 5.9745E-10 | 5.4703E-10 | 1.9113E-10 | 3.8653E-11 | 8.8149E-11 | 2.0637E-11 |
| 2.8000E+01 | 5.1689E-10 | 9.6729E-11 | 6.4633E-10 | 5.9194E-10 | 2.1316E-10 | 4.4698E-11 | 9.5794E-11 | 2.2515E-11 |
| 3.0000E+01 | 5.5381E-10 | 1.0364E-10 | 6.9521E-10 | 6.3686E-10 | 2.3552E-10 | 5.0887E-11 | 1.0344E-10 | 2.4397E-11 |
| 3.2000E+01 | 5.9073E-10 | 1.1055E-10 | 7.4408E-10 | 6.8177E-10 | 2.5813E-10 | 5.7197E-11 | 1.1108E-10 | 2.6282E-11 |
| 3.4000E+01 | 6.2765E-10 | 1.1746E-10 | 7.9294E-10 | 7.2668E-10 | 2.8093E-10 | 6.3600E-11 | 1.1872E-10 | 2.8168E-11 |
| 3.6000E+01 | 6.6457E-10 | 1.2437E-10 | 8.4180E-10 | 7.7160E-10 | 3.0389E-10 | 7.0074E-11 | 1.2636E-10 | 3.0057E-11 |
| 3.8000E+01 | 7.0149E-10 | 1.3127E-10 | 8.9065E-10 | 8.1651E-10 | 3.2696E-10 | 7.6604E-11 | 1.3401E-10 | 3.1947E-11 |
| 4.0000E+01 | 7.3841E-10 | 1.3818E-10 | 9.3950E-10 | 8.6143E-10 | 3.5012E-10 | 8.3176E-11 | 1.4165E-10 | 3.3838E-11 |
| 4.2000E+01 | 7.7533E-10 | 1.4509E-10 | 9.8835E-10 | 9.0635E-10 | 3.7335E-10 | 8.9782E-11 | 1.4929E-10 | 3.5729E-11 |
| 4.4000E+01 | 8.1225E-10 | 1.5200E-10 | 1.0372E-09 | 9.5127E-10 | 3.9663E-10 | 9.6412E-11 | 1.5693E-10 | 3.7622E-11 |
| 4.6000E+01 | 8.4917E-10 | 1.5891E-10 | 1.0860E-09 | 9.9618E-10 | 4.1995E-10 | 1.0306E-10 | 1.6457E-10 | 3.9514E-11 |
| 4.8000E+01 | 8.8609E-10 | 1.6582E-10 | 1.1349E-09 | 1.0411E-09 | 4.4330E-10 | 1.0973E-10 | 1.7221E-10 | 4.1407E-11 |
| 5.0000E+01 | 9.2301E-10 | 1.7273E-10 | 1.1837E-09 | 1.0860E-09 | 4.6668E-10 | 1.1640E-10 | 1.7984E-10 | 4.3301E-11 |
| 5.2000E+01 | 9.5994E-10 | 1.7964E-10 | 1.2326E-09 | 1.1309E-09 | 4.9007E-10 | 1.2309E-10 | 1.8748E-10 | 4.5194E-11 |
| 5.4000E+01 | 9.9686E-10 | 1.8655E-10 | 1.2814E-09 | 1.1759E-09 | 5.1348E-10 | 1.2978E-10 | 1.9512E-10 | 4.7088E-11 |
| 5.6000E+01 | 1.0338E-09 | 1.9346E-10 | 1.3303E-09 | 1.2208E-09 | 5.3690E-10 | 1.3647E-10 | 2.0276E-10 | 4.8981E-11 |
| 5.8000E+01 | 1.0707E-09 | 2.0037E-10 | 1.3791E-09 | 1.2657E-09 | 5.6033E-10 | 1.4317E-10 | 2.1040E-10 | 5.0875E-11 |
| 6.0000E+01 | 1.1076E-09 | 2.0728E-10 | 1.4280E-09 | 1.3106E-09 | 5.8376E-10 | 1.4988E-10 | 2.1804E-10 | 5.2769E-11 |
| 6.2000E+01 | 1.1445E-09 | 2.1419E-10 | 1.4768E-09 | 1.3555E-09 | 6.0720E-10 | 1.5658E-10 | 2.2568E-10 | 5.4663E-11 |
| 6.4000E+01 | 1.1815E-09 | 2.2109E-10 | 1.5256E-09 | 1.4004E-09 | 6.3064E-10 | 1.6329E-10 | 2.3332E-10 | 5.6557E-11 |
| 6.6000E+01 | 1.2184E-09 | 2.2800E-10 | 1.5745E-09 | 1.4454E-09 | 6.5408E-10 | 1.7000E-10 | 2.4096E-10 | 5.8451E-11 |
| 6.8000E+01 | 1.2553E-09 | 2.3491E-10 | 1.6233E-09 | 1.4903E-09 | 6.7753E-10 | 1.7671E-10 | 2.4860E-10 | 6.0345E-11 |
| 7.0000E+01 | 1.2922E-09 | 2.4182E-10 | 1.6722E-09 | 1.5352E-09 | 7.0098E-10 | 1.8342E-10 | 2.5624E-10 | 6.2239E-11 |
| 7.2000E+01 | 1.3292E-09 | 2.4873E-10 | 1.7210E-09 | 1.5801E-09 | 7.2442E-10 | 1.9013E-10 | 2.6388E-10 | 6.4133E-11 |
| 7.4000E+01 | 1.3661E-09 | 2.5564E-10 | 1.7699E-09 | 1.6250E-09 | 7.4787E-10 | 1.9684E-10 | 2.7152E-10 | 6.6027E-11 |
| 7.6000E+01 | 1.4030E-09 | 2.6255E-10 | 1.8187E-09 | 1.6700E-09 | 7.7133E-10 | 2.0355E-10 | 2.7916E-10 | 6.7922E-11 |
| 7.8000E+01 | 1.4399E-09 | 2.6946E-10 | 1.8675E-09 | 1.7149E-09 | 7.9478E-10 | 2.1026E-10 | 2.8679E-10 | 6.9816E-11 |
| 8.0000E+01 | 1.4768E-09 | 2.7637E-10 | 1.9164E-09 | 1.7598E-09 | 8.1823E-10 | 2.1697E-10 | 2.9443E-10 | 7.1710E-11 |
| 8.2000E+01 | 1.5138E-09 | 2.8328E-10 | 1.9652E-09 | 1.8047E-09 | 8.4168E-10 | 2.2368E-10 | 3.0207E-10 | 7.3604E-11 |
| 8.4000E+01 | 1.5507E-09 | 2.9019E-10 | 2.0141E-09 | 1.8496E-09 | 8.6513E-10 | 2.3040E-10 | 3.0971E-10 | 7.5498E-11 |
| 8.6000E+01 | 1.5876E-09 | 2.9710E-10 | 2.0629E-09 | 1.8946E-09 | 8.8858E-10 | 2.3711E-10 | 3.1735E-10 | 7.7392E-11 |
| 8.8000E+01 | 1.6245E-09 | 3.0400E-10 | 2.1118E-09 | 1.9395E-09 | 9.1204E-10 | 2.4382E-10 | 3.2498E-10 | 7.9286E-11 |
| 9.0000E+01 | 1.6614E-09 | 3.1091E-10 | 2.1606E-09 | 1.9844E-09 | 9.3549E-10 | 2.5053E-10 | 3.3263E-10 | 8.1180E-11 |
| 9.2000E+01 | 1.6984E-09 | 3.1782E-10 | 2.2094E-09 | 2.0293E-09 | 9.5894E-10 | 2.5725E-10 | 3.4027E-10 | 8.3074E-11 |
| 9.4000E+01 | 1.7353E-09 | 3.2473E-10 | 2.2583E-09 | 2.0742E-09 | 9.8239E-10 | 2.6396E-10 | 3.4791E-10 | 8.4969E-11 |
| 9.6000E+01 | 1.7722E-09 | 3.3164E-10 | 2.3071E-09 | 2.1192E-09 | 1.0058E-09 | 2.7067E-10 | 3.5555E-10 | 8.6863E-11 |
| 9.8000E+01 | 1.8091E-09 | 3.3855E-10 | 2.3560E-09 | 2.1641E-09 | 1.0293E-09 | 2.7739E-10 | 3.6319E-10 | 8.8757E-11 |
| 1.0000E+02 | 1.8461E-09 | 3.4546E-10 | 2.4048E-09 | 2.2090E-09 | 1.0528E-09 | 2.8410E-10 | 3.7083E-10 | 9.0651E-11 |

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